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Factors affecting breakthrough time of commercial pesticide formulations through butyl glove material

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FACTORS AFFECTING BREAKTHROUGH TIME OF COMMERCIAL PESTICIDE FORMULATIONS THROUGH BUTYL GLOVE MATERIAL

by

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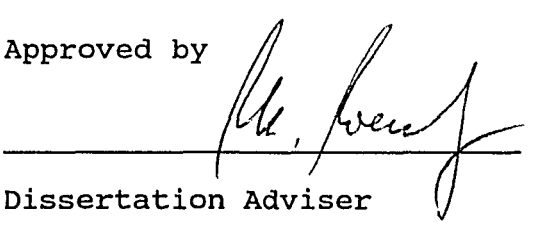

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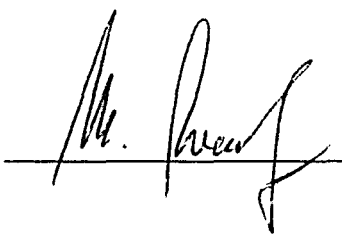
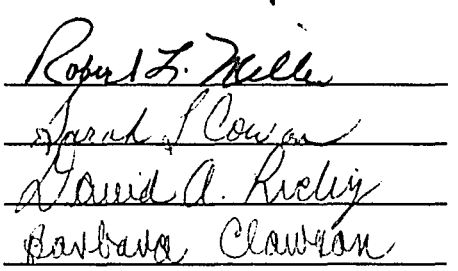
Dissertation Adviser 

Committee Members 

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Very little permeation work has addressed the breakthrough of a complex mixture such as a commercial pesticide formulation through protective glove materials. To evaluate the factors that affect the breakthrough time of the pesticide active ingredient, the ASTM permeation cell system was used with two thicknesses of butyl rubber, three common pesticide commercial formulations and elevated temperatures (35°C, 45°C, 55°C).

It was found that polymer/solvent interaction, glove thickness, and temperature play a crucial role in breakthrough time. Where the Hansen 3-dimensional solubility parameters of the glove polymer and pesticide formulation solvent were similar the breakthrough time of the active ingredient was practically instantaneous regardless of glove thickness and temperature. Degradation was the primary breakthrough mechanism.

A second mechanism, diffusion, occurred when the solubility parameters did not match, and was caused by the concentration gradients on either side of the polymeric barrier. Temperature and glove thickness were important factors in the breakthrough time. Each glove thickness exhibited a unique breakthrough time pattern and an Arrhenius type relationship. The thin glove exhibited

lower breakthrough times than the thick glove for the same temperatures. The activation energy of diffusion from the Arrhenius relationship could be determined from the slope of the reciprocal breakthrough time against the reciprocal of the temperature in degrees Kelvin.

The calculated activation energy of the thick glove was less than the thin glove. This phenomenon illustrated that the glove thickness, when increased sufficiently, minimized the effect of temperature on the breakthrough time.

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CHAPTER 1

INTRODUCTION

Garments designed specifically for the protection of the human body have become widespread in recent years with increases in the production, use and waste disposal of hazardous chemicals. Exposure to these substances can cause "nocuous effects on humans such as dermatitis, burns, or serious degenerative diseases like cancer or pulmonary fibrosis" (1). Since it is not always possible to eliminate all exposure by environmental control, there is a need for protective clothing to prevent direct contact of the skin with the hazardous chemical. Serious injury and even death may result from short exposures of skin to high concentrations of very toxic substances (24).

Gloves are a crucial part of the protective clothing ensemble. Hands are the part of the body most likely to come in contact with the chemical and may act as a conduit into the human system. Lacerations or open wounds on the hand increase the possibility of a toxic substance entering the body. If a toxic liquid or vapor permeates a glove and touches the skin, one of four things will happen:

1. The skin may act as a barrier such that the substance cannot enter or penetrate.

2. The substance may penetrate the skin surface.
3. The substance may penetrate the skin surface and injure the skin tissues.
4. The substance may penetrate the skin, enter the blood stream and be disseminated through the body to perhaps injure various parts of it (24).

In order to evaluate dermal exposure to potentially hazardous liquids, chemical permeation measurements of protective materials are made. Two important parameters are obtained: breakthrough time and steady-state permeation rate. Breakthrough time serves as an estimation of the protection provided by the protective clothing. The steady-state permeation rate permits quantitative analysis of the amount of hazardous liquid to which the skin is exposed. (4)

Along with the increase in permeation testing, the need for a standard test method has become evident. In 1981 the American Society for Testing and Materials (ASTM) adopted a standard method for testing the chemical permeation of a protective material. To date most permeation studies have involved analytical grade chemicals, used in industry and laboratory situations, as the challenge solutions. Data bases containing this type of information are now available. However, very little permeation data regarding mixtures have been collected and

there are no published studies investigating pesticide permeation per se.

The importance of evaluating pesticide permeation through a membrane has been recognized and discussed by Hartley and Graham-Bryce (14, 15). Their discussion however is limited to the solubility of the pesticide in soil, diffusion through leaves and plants, and permeation through skin (14). Permeation through polymeric material is not addressed directly.

The purpose of this study is to determine the effects of temperature and glove thickness on permeation breakthrough time using different pesticide formulations. The objectives of this study are:

1. Determine the breakthrough time of the pesticide formulations through protective gloves of butyl rubber.
2. Study the effect of three different pesticide formulations on the breakthrough time.
3. Determine if an increase in temperature gives a lower breakthrough time.
4. Determine if a decrease in glove thickness gives a lower breakthrough time.
5. Determine if there is interaction among the three independent variables that affect the breakthrough time significantly.

Pesticide formulations are complex materials. Protective glove performance characteristics against such formulations are unknown at the present time. This study initiates the development of a useful data base for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 PROTECTIVE GLOVES

Gloves are one of the most important defenses against harmful chemicals; however, they are only a supplement to good industrial practices. The National Safety Council states that gloves should be the "last approach considered to provide employees with protection against skin contact with chemicals" (33). This approach is appropriate for chemicals that are not skin absorbable, poisonous, or sensitizers. With the skin absorbable chemicals, gloves should always be worn as a precaution.

The Safety Council has published "Selection and Use Guidelines for Chemically Impervious Gloves". These guidelines offer general criteria for selecting an appropriate glove material for the chemical in question. The list of points, however only guides in a selection decision. (Appendix A) If the challenge chemical is a solvent or single agent, most of the data on which to base the selection decision, can be obtained from Material Safety Data Sheets (MSDS) and the glove manufacturers' published permeation literature (33).

Currently, to help the layman determine an appropriate glove polymer which will resist permeation by a chemical, many glove manufacturers such as North, Edmont and Pioneer publish chemical resistance charts. These charts rate each material on how it will act in specific chemicals (from "no effect", to "complete destruction" or permeation breakthrough times) (29).

In addition to the manufacturers' data there are recently published studies in publications such as the American Industrial Hygiene Association Journal concerning the permeation of chemicals through protective clothing made from polymer based materials. ASTM committee F-23 has developed a standard for permeation testing of protective clothing F739-81 using a permeation cell. It was updated to F739-85 in 1985 (1). The ASTM permeation cell has subsequently been used to generate most of the published information that has been made available to the industrial hygienist.

This body of information has several shortcomings for the person selecting the glove. The chemical resistance charts are only guidelines, various factors (such as heat, abrasion, concentration or composition of solution) will affect the glove's performance. There is no permeation data for some generic glove types. The data developed from one glove thickness is not useful for other glove

thicknesses. Consequently, the decision making process requires interpretation of sometimes incomplete data. (24)

It is universally recommended that the selected glove polymer be tested for its particular application under simulated use conditions to ensure its suitability. This criterion for evaluation is especially critical for chemicals where permeation data is not currently available. (24, 33)

Gloves chosen based on the best permeability resistance may not always be the best overall choice. A glove choice should reflect the optimum of all relevant factors: permeation; durability; dexterity; tactile sensitivity; friction; wearing schedule (all day, short term/frequent); and cost. Unfortunately, these factors are often in conflict eg., glove thickness favors reduced permeability and improved durability, but may compromise dexterity and touch (33). The loss of tactile sensitivity during glove use may result in glove contamination without the wearer's knowledge. This loss increases the risk of area contamination, personal exposure and detrimental health effects. While the glove is worn, other precautions such as rinsing are recommended every half-hour and after high-potential contact operations. Even carefully selected gloves may fail with continued chemical contact. (33)

Therefore selecting gloves for specific tasks is usually a trial and error process. If pain or dermatitis develop a different glove must be substituted. This process must be repeated until a satisfactory glove is found. To date, attempts to determine a glove's effectiveness from known basic principles have been hampered by either the lack of fundamental permeation data or large errors occurring because of unknown interaction between a solvent and glove polymer. Additionally, many gloves are bonded in layers or to inner liners thus compounding the problem. (23)

The barrier properties of protective gloves to chemical permeation is the primary concern in the selection process. A large fraction of the experimental work has focused on the permeation of a single chemical in the challenge liquid. The results of such testing are useful for the purpose of broadly characterizing the effectiveness of the large variety of commercially available glove materials. Many of the liquids to which workers may be exposed, however, are multi-component rather than single-component in composition (12).

Multi-component solutions can be more aggressive in their permeation behavior than are pure chemicals. One component may promote the permeation of other components or the overall harmful health effect may be greater than

for any one component alone. At the present time, there are no generally applicable methods for predicting thepermeation properties of multi-component liquids. Efforts toward this objective are in their preliminary stages and typically have been based on the solubility parameter theory (12). Relative to the preponderance of multi-component solutions in industry, the availability of data on the barrier effectiveness of protective clothing to such solutions is minimal (13).

Currently the glove types that are available fall into these categories: natural rubber, neoprene, nitrile, polyvinyl chloride, butyl, polyvinyl alcohol, and Viton. Even though Viton is a trade name for the Dupont Company's hexafluoropropylene-tetrafluorethane copolymer, it is considered a class of glove polymer by itself (24). Among the most effective types of industrial gloves are those made from Viton, butyl elastomers and nitrile latex.

Viton gloves protect workers handling chlorinated and aromatic solvents. Workers not properly protected from such chemicals run a greater than normal risk of contracting dermatitis or other skin ailments. This polymer glove can be used in applications such as aircraft maintenance, hazardous waste handling, chemical and automotive industries and degreasing operations. Viton

gloves also provide effective hand protection for workers handling benzene, a suspected carcinogen often linked with leukemia. In permeation resistance testing, they were found to provide up to six hours of total protection against benzene. In addition, they can be used in or around water and water-based solutions (24).

Nitrile latex provides excellent puncture and abrasion resistance, and also protects against commonly used industrial chemicals such as petroleum solvents, oils, grease and amino acids. In permeation resistance testing, nitrile latex gloves were found very effective against cyclohexanol, formaldehyde (37% in water), hydrazine (70% in water) and pentachlorophenol powder fungicide (1% in kerosene.) All of these chemicals are known skin irritants. (24)

Neoprene is a substituted isoprene, the methyl group is substituted with a chlorine atom. This polymer is suitable for oils, waxes, grease, petroleum products, aliphatic hydroxy compounds, aliphatic hydrocarbons, and alcohols (29). Butyl gloves are ideal for workers handling ketones and esters (24).

2.2 PERMEATION ANALYSIS

2.2.1 Previous Studies

Most of the challenge solutions reported in the literature are pure reagents. These studies typically

consist of some generic glove types evaluated against several challenge solutions at 25°C. Some of the variables that have arisen from these permeation studies are the thickness of the glove, temperature of permeation experiment, and types of challenge solutions.

Studies such as Stampfer's "Permeation of Eleven Protective Garment Materials by Four Organic Solvents" (35), Schwope's "Dimethyl Sulfoxide Permeation through Glove Materials" (32), Vahdat's "Permeation of Polymeric Materials by Toluene" (35) and Sansone's "The Permeability of Laboratory Gloves to Selected Solvents" (30), illustrate the types of solvent permeation studies done with several glove or material types. While these studies have recognized value for characterizing the general permeation properties of gloves, their specific results do not have direct relevancy in this pesticide study.

To address specific glove permeation problem areas, several studies have been performed. Mickelson and Hall addressed the question of gloves made of the same generic polymer by different manufacturers. The hypothesis of this study was that glove products bearing the same generic name, but produced by different manufacturers, would yield the same breakthrough times. In making important comparisons between glove types, the researchers

compared polymeric materials of different thicknesses. The comparison was made on the absolute breakthrough times, not times that were corrected for the differing thicknesses of the materials. The significant difference in chemical breakthrough times reported among generically similar products produced by different manufacturers may be due to glove thickness. Because of these findings, the permeation results of one product cannot be extended to other manufacturers's products bearing the same generic material name. Consequently substituting generically equivalent gloves for gloves that had proven protection may lead to unexpected exposures. Each product needs to be tested independently. (23)

In an attempt to quantify the behavior of challenge solution mixtures, three solvents were combined in various binary combinations (21). Each component's breakthrough time was determined separately, then the breakthrough and steady-state permeation rate were determined for the mixture solutions. Mikelson et al (21) found an increased risk of exposure as a result of early breakthrough times, and a higher mixture permeation rate over that of the pure chemical permeation. The solvents used in the mixtures were selected from common industrial solvents. These mixes were toluene and p-xylene, n-butyl acetate and methanol, n-hexane and methyl ethyl ketone. The

permeation of protective barriers by binary mixtures may increase the potential chemical exposure of employees (over that of the pure chemical components) in three ways:

1. It may decrease the breakthrough time of the components.
2. A component that does not permeate in its pure form may be transported through the barrier by another component in the mixture.
3. The collective permeation rate of the mixture may be higher than any pure component permeation rate. (21)

In order to examine the data further, the solubility parameter theory is a way to estimate permeation characteristics (24). Forsberg and Faniadis (12) used this theory in a study which addressed multi-component mixtures. They not only looked at 13 different solution mixtures against 13 glove compositions, but they used a modified procedure. The solutions were selected to be representative of those in segments of the chemical and aircraft industries. The ASTM cell was used in a horizontal position rather than the vertical position. The glove specimen was removed after a 4-hour test, wiped with filter paper and dried at room temperature for 20 hours. Then the specimen was subjected to a second permeation test as a simulation of reuse (12).

The selection of the glove specimen/solution pairs tested in this study was guided by the solubility

parameter theory. The parameters used for this study were based on the hydrogen bonding of the polymers and solvents. Solubility parameters for the glove specimens were approximated from tabulations of values as presented in Barton (2). Solubility parameters for the solutions were calculated on the basis of the parameters for the pure chemical and the assumption that parameters are additive on a volume percentage basis. In general the focus of the work was on glove material/chemical combinations in which the parameter for the glove material differed significantly from that of the solution. Such materials would be expected to exhibit better barrier properties than those having solubility parameters close to those of the solutions (12).

The solubility parameter theory provided one basis for discussion of the research. In general the multi-component solutions can be characterized as having intermediate solubility parameters in the range of 19.5 to 22.5 $MPa^{1/2}$ with moderate hydrogen bonding. Published values for butyl rubber are in the range of 15 to 16 $MPa^{1/2}$ and the polymer has little or no hydrogen bonding. On the other hand, the polyvinyl alcohol has a high solubility parameter in the range of 25 to 26 $MPa^{1/2}$ and of course, has a high degree of hydrogen bonding. According to the

theory, materials differing significantly in solubility parameter from that of the chemical or mixture of chemicals are likely to be resistant to the liquid. In general this premise was found to be true. (12)

Interestingly, Viton, neoprene and nitrile with solubility parameters in the range of 18 to 20 MPa $^{1/2}$ exhibited poor resistance to the challenge solutions. The ketones, acetates and aromatics present in most of the multi-component solutions may account for the poor performance of these materials because they also have solubility parameters in this range.

Multi-component solutions represent a significant fraction of the challenges likely to be experienced by chemical protective clothing. It is impractical to think that testing can be performed for all the possible combinations of chemicals that might be found in for example, the aircraft industry or in the cleanup of hazardous wastes. The solubility parameter theory offers a promising approach to preliminary selection of candidate protective materials for testing and a framework for data analysis. For example, PVA and butyl rubber represent opposite ends of the solubility parameter spectrum; one or the other material would seem to be an effective barrier to a widely divergent group of multi-component and pure solutions (12).

Most of these previous experiments were carried out at 25°C, but two permeation tests varied the temperature to determine its affect on permeation. Vahadt (36) evaluated the permeation characteristics of 4 glove polymers by toluene at 25 and 45°C. His efforts show that an increase in the temperature increases the steady-state permeation rate by 70% to 100% in the case of butyl nomex and butyl rubber respectively. However neoprene, which has the highest permeation rate at room temperature, shows a smaller change (14%) in the permeation rate when the temperature increased to 45°C. (36) Going to the other end of the temperature range, a study done for the Coast Guard also took temperature into consideration by using 0°C in addition to 25°C. The 0°C was to simulate the cold water that might be encountered. It was found that the decrease in temperature significantly decreased the chemical breakthrough times. (23)

2.2.2 Solubility Parameters

The evaluation of permeation characteristics may involve the calculation of a value called the solubility parameter. This value is dependent upon the method used but it always represents the solubility characteristic of the liquid or solid being evaluated. Therefore, a liquid that has a total solubility parameter with polarity and hydrogen bonding characteristics similar to a polymer will

be a solvent for that polymer. Until 1967, only the total solubility parameter, calculated from the heat of vaporization, was considered in experiments (10, 11). This relationship is:

$$\delta^2 = (\Delta H_v - RT)/V_m$$

where H_v = heat of vaporization
R = gas constant
T = temperature in degrees Kelvin
V_m = the molar volume

The Hildebrand-Scatchard method is a well known technique which uses the heat of mixing to calculate the parameter (2). Use of this theoretical solubility parameter has declined in recent years as interest has increased in the practical application chemistry and more sophisticated solution theories such as Hansen's (3, 13). In 1967, Hansen modified the Hildebrand parameter by dividing it into 3 sub-components where the polarity, hydrogen-bonding and dispersion forces were all taken into account when characterizing solubility. These components can be calculated by using the molar volume and energy or molar attraction constants. The equations for dispersion, hydrogen-bonding and polarity forces are respectively:

$$\delta_d = \Sigma F_d/V_m \qquad \text{Eq. (1)}$$

$$\delta_h = \sqrt{(\Sigma E_h/V_m)} \qquad \text{Eq. (2)}$$

$$\delta_p = \sqrt{(\Sigma F_p)}/V_m \qquad \text{Eq. (3)}$$

where F is the group molar attraction constant and E is the cohesion energy. This modification is called the Hansen 3-dimensional solubility parameter (13).

Although several groups of investigators have been working on the problem of proper protective clothing selection, a complete picture of the factors affecting permeation of clothing materials has not yet emerged. A method based on the three-dimensional solubility parameter was developed by Perkins (28).

Usually, permeation has been regarded as a three-stage process. First, the challenge solution dissolves into the membrane, diffuses across the membrane then finally evaporates from the opposite side. In effect, permeation is mainly a function of solubility and diffusability through the polymer, while evaporation plays a small role (28).

Several things can occur to alter this physical process. These include the chemical reaction or molecular interactions of the challenge solution with the polymer or the non-polymer additives which make it more elastic or economical. The solubility step is dependent upon the molecular interactions between chemical and polymer, and it may be the most important step in the permeation process. Furthermore, the diffusion step can be altered from a straightforward Fickian behavior (diffusion by

concentration gradient) to a solution-polymer interaction (so-called non-Fickian diffusion). Hence, the molecular interactions may be most important in the permeation process. They may also be the key to predicting breakthrough times, permeation rates or other permeation parameters. (28)

In 1967, Hansen (13) proposed that the solubility parameter for any compound (i.e. the square root of the sum of forces that hold the molecules together, also known as total cohesive energy) is composed of four factors or forces. He considered three of these to be most important. The first factor is the London or dispersion force (D) which is entirely quantum mechanical in origin and leads to instantaneous dipoles in otherwise non-polar molecules. This factor is the only force contributing to the solubility parameter for a saturated, non-polar hydrocarbon such as pentane (28).

The second force (P) is due to permanent dipoles of polar molecules such as water and is often attributed to exposed oxygen, fluorine or nitrogen atoms. The third force (H) is due to hydrogen bonding, that is, bonds formed between protons and unshared electrons of another molecule. This force also occurs in polar compounds such as water; however, the presence of a dipole does not

necessarily yield hydrogen bonding of a given magnitude or vice versa.

The relationship to the overall solubility parameter (S) or total cohesive force is given by:

$$S^2 = D^2 + P^2 + H^2 \qquad \text{Eq. (4)}$$

where the symbols are as defined above. The total cohesive force or square of the solubility parameter is the sum of squares of these three forces and determines the energy $[(J/cc)^{1/2}]$ holding the molecules together. The three-dimensional solubility parameter (3-dsp) can be considered as a 3- dimensional vector with coordinates D,P,H (28, 32).

Hansen did solution experiments whereby solvents and polymer resins were mixed and the degree of solubility was assessed qualitatively. He plotted the three parameters in 3 dimensions (3D) for all solvents tested. Around the total volume represented by very "good" solvents of a particular resin (i.e. a clear solution) he constructed a sphere. In order to cause the volume to be a sphere, he had to double the dispersion scale of the axis. There is no theoretical explanation for this adjustment. Almost all solvents lying inside the sphere would dissolve the resin while outside the sphere there was generally no solution or a poor solution. The same experiment can be performed for cured polymers if the variable determining

the radius and center of the sphere is swelling or weight gain of the polymer specimen, rather than degree of solubility (swelling is equal to 25% weight gain) (28).

Another method, which is used in the laboratories at the University of Alabama in Birmingham (26) (28), is based on the assumption that the polymer weight gain will increase as the difference in the solubility parameter numbers between the polymer and the solvent decreases. They use a computer to plot the parameters in 3D and analyze the correlations between parameters. This method and a two-dimensional plotting technique give similar results (28).

The two dimensional technique involves plotting the two parameters of the solvents on three graphs. One graph would have polarity by hydrogen bonding, another would plot polarity by dispersion and the third would plot dispersion by hydrogen-bonding. The coordinates from the polymer weight gain would be averaged to approximate a value for each parameter.

Although Hansen was looking for good solvents for paints and inks, his general methods can be applied to the selection of the best glove material for particular solvents. This approach has been promoted by Spence using only the total solubility parameter, without regard for its three component values. Spence's preliminary work

showed that the difference between the total solubility parameters of the polymer and the solution had potential for predicting breakthrough time. In other words the closer the two total solubility parameters were to one another, the quicker the breakthrough time (28).

Others have used the solubility parameter theory somewhat differently. By immersing polymers in solvent solutions for a period of time and then measuring the weight gain of the polymer (the amount of solvent absorbed) the relative solubility of the two compounds may be determined. The greater the weight gain, the greater the solubility. ; Although it appears that weight gain should be a fairly good predictor of permeation parameter, there are some exceptions as reported by Coletta et al. (25) His findings suggest that high weight gain predicted short breakthrough time and high permeation rate, but the opposite was not necessarily true. In certain cross-linked polymers, smaller weight gains were recorded, but the solvent did dissolve the polymer (28).

An experiment by Nunn indicates that the boundary of the solubility sphere is not a clear-cut division between solvents and nonsolvents (2). Particular caution should be exercised when there are significant donor-acceptor interactions. Although Lewis acid-Lewis base interactions are not fully treated by the Hansen parameter formalism,

the 3-dsp parameter approach is often adequate for practical purposes. Extension of cohesion parameters to Lewis acid and Lewis base components for polymers is still rare, except in the characterization of chromatographic materials (2).

Henriksen has correlated the 3 dsp with permeation rate and breakthrough time (28). He used the relationship

$$A = [4(D_p - D_s)^2 + (H_p - H_s)^2 + (P_p - P_s)^2]^{1/2}$$

where the p and s subscripts represent the polymer and solvent respectively. The coefficient 4 or 2^2 is used to produce the spherical solubility region as described earlier. A is an estimate of the interaction of the two compounds and represents the distance between two points in three dimensional space. As A increases, the permeation rate should decrease and breakthrough time should lengthen. In nine correlation studies of A versus permeation rate involving five polymers Henriksen reported correlations ranging from poor ($r = -0.5$) to excellent ($r = -0.9$). The permeation rate used for this analysis was taken from previous work by Nelson et al (23). Henriksen applied the 3D solubility parameters for the polymers, which had been derived by Hansen for the raw or non-polymerized resin materials (28). The resulting poor correlation might be due to the inconsistency of the polymers used in the two sets of data. These solubility

parameter and permeation rate values might have been mismatched due to the time difference between the two studies. In this time the processing techniques of the polymers could have changed thereby creating a problem of like-named but unlike-composition polymers being compared for the correlation.

It would be useful if manufacturers would begin to determine and publish 3-dsp values for their products. Even though 3-dsp values consider more of the factors in permeation mechanisms than do other methods, they are not the complete answer for predicting glove behavior. Other factors figure into the permeation process such as size and shape of solvent molecule, and crystallinity of the polymer. Another consideration is that some compounds appear to have properties that are not predicted by the 3-dsp approach. Perhaps in these exceptions, other factors such as molecular size and temperature become more important (28).

An example of the 3-dsp calculation is the purpose of a work by Perkins et al (27). He calculated the 3-dsp of the DuPont polymer Viton. In addition, a method for qualitatively predicting the appropriateness of Viton for a given solvent was discussed as well as its possible application to other polymers (27).

Previously, Viton was shown to be highly resistant to permeation by straight chain hydrocarbons, aromatic hydrocarbons, and chlorinated solvents. Since these compounds make up a large portion of solvents used, Viton often had been thought of as a superior polymer material for protection from solvents. Because it is a fluorocarbon, Viton is polar. Because it does not interact significantly with nonpolar solvents, it has low solubility and permeation rates. On the other hand,it does interact with polar solvents, particularly ketones. (27)

This study consisted of gloves of Viton and reagent grade solvents. A solubility test was performed to determine the 3-dsp solubility parameters. These parameters were determined by placing small pieces of the polymer (2 cm diameter) in separate vials, each containing about 10 ml of one of approximately 55 different solvents. The material remained in the solvent for a period of 14 days. Specimen weight was measured prior to placing the material in the solvent and again after removing the material from the solvent. Upon removal from the solvent, the polymer material was quickly blotted dry and weighed. All tests were performed in duplicate. (27)

In order to determine the 3-dsp for Viton the 3-dsp data for each solvent were placed on two dimensional plots

as follows: hydrogen bonding versus polarity, hydrogen bonding versus dispersion, and dispersion versus polarity. After plotting points, an attempt was made to draw concentric circles around all points or solvents having greater than 10%, 20% or 50% weight gain in each of the plots.

The two-coordinate center of each circle in each plot was determined and the values for each factor averaged. In other words, an imaginary solvent with a 3-dsp value equivalent to the averaged center should have an infinite weight gain or total solution of a non-crosslinked polymer (27). The second part of the study involved testing the permeation of several Viton-solvent combinations. The ASTM procedure was used and analysis performed with either an infrared analyzer or gas chromatograph (27).

From this study, a method for predicting breakthrough times and permeation rate values for Viton was demonstrated. While quantitative predictions were not possible, the resulting qualitative predictions can be used to speed glove selection and reduce the number of necessary permeation tests. However "further work is necessary to improve the prediction accuracy of the model, construct models for other polymers, and investigate the applicability of 3-DSP for mixtures to the model" (27).

2.2.3 Experimental Method

There are three common approaches in permeation experimentation when using the cell permeation method:

1. The dynamic system which uses a continuous flow of fresh collecting medium.
2. A closed system which does not lose a significant volume of the collection solution when samples are extracted.
3. The closed system which does have a significant volume loss from sampling. (40)

Each will be briefly discussed in the following paragraphs.

In a dynamic system a continuous flow of fresh collecting medium transports the permeated challenge solution from the collection side of the test cell to the analyzer. This is the open system or the open loop system. The collection medium can be either a liquid or a gas and the chosen monitoring instrument should be suitable for this type of continuous analysis. Total hydrocarbon analyzers, infrared analyzers, and monitoring instruments designed for a specific compound have been used to develop a profile of the concentration in the collection medium (40).

To calculate the permeation rate of the challenge solution in a dynamic system the following expression is used:

$$P = C\ F/A$$

where: A = the area of the exposed material
C = the concentration of chemical in the collection side at time T (mg/L)
F = flow rate of fresh collecting medium through the cell (L/min)
P = permeation rate (mg/cm^2 min)

The concentration of the challenge solution in the collection medium is directly proportional to the permeation rate by the factor of F/A.

One experimental method of a closed system dictates withdrawal of extremely small discrete samples from the collection side. The samples may be analyzed by a non-destructive technique then replaced in the collection side of the cell before further sampling. Another option is withdrawing a sample of insignificant volume in relation to the total collection volume (ex. μl aliquots). As long as the entire surface of the glove is in contact with the collection solution, withdrawn samples may be analyzed by a destructive technique and need not be replaced. (40)

The permeation rate for the above technique can be calculated:

$$P = \frac{(C_i - C_{i-1})V_r}{(T_{i-T_{i-1}})A}$$

where: C = concentration of chemical in the collection side at time T, (mg/L)
i = an indexing number assigned to each sample (ex.: i=1)

T = Time elapsed beginning with the initial chemical contact, where T_i is the time at which the discrete sample, i, was removed, (min)

V_t = total volume of the collection medium, (L)

In the second experimental method used with a closed system samples are not replaced in the cell. If these samples are of a significant quantity, then the equation below must be used. It has a correction term for the reduced volume of the collection medium.

$$P = \frac{(C_i - C_{i-1})[V_t - (i-1)V_s]}{(T_{i-Ti-1})A}$$

where: V_s = Volume of the sample removed from the collection medium (L)

If it is necessary to add a volume of fresh collection medium to the cell after each discrete sample is taken to keep the glove sample in contact with the collection medium, a correction term is needed in the equation. In this case, the total volume remains constant but the concentration of challenge solution in the collection medium at T_{i-1} must be corrected by the amount it is diluted: $[V_t - V_s]/V_t$. Consequently the formula becomes:

$$P = \frac{\frac{C_i - C_{i-1}(V_t - V_s)}{V_t}}{(T_{i-Ti-1})A}$$

In all equations for discrete sampling it is important to note that the calculated permeation rate is the average

permeation rate over the time period since the last sample was taken, T_{i-1} to T_i, and not the permeation rate at the time the discrete sample was taken. (34)

The ASTM method of permeation analysis plots the concentration of chemical in collection medium versus time. There are some drawbacks. When using the ASTM permeation method, the concentration of challenge chemical in the collection medium is proportional to the total volume of collection medium. Therefore, the data on the plot cannot be compared between laboratories or converted into units that may be meaningful to the researcher because the report does not include the total volume of the collection medium. (40)

Winter has suggested an improved method for providing a graphical representation of the data by plotting the permeation rate versus time. The advantage of this plot is the relative ease for the readers' interpretation of the data since it is in units relevant to the users of the information and directly comparable to plots from other laboratories using another experimental setup. (40)

CHAPTER 3

METHODOLOGY

3.1 DESIGN

Because the mechanism of commercial pesticide mixture permeation is very complex, the purpose of this study was to qualitatively analyze some of the suspected factors that affect breakthrough times. This work may serve as a basis for other studies which concentrate on one or more of these factors. The 3 x 2 x 2 factorial design had the independent variables of pesticide formulation 3 levels; temperature 2 levels; and glove thickness 2 levels.

This project involved 2 stages: the permeation experiments and the solubility parameter determinations. For the permeation segment, breakthrough times were determined using the 2 glove thicknesses and 3 pesticide formulations under 2 temperatures using the ASTM test method 739-85.

The general permeation procedure had three replications of each experiment for the diazinon and metolachlor, and two replications for atrazine. An experiment consisted of a glove material tested at two temperatures: 45 and 35 °C using a controlled temperature

water bath. Twenty five degrees Centigrade represents the standard testing condition. Under ordinary glove use, temperatures would be higher than 25°C due to body heat and atmospheric conditions. Therefore, the two higher temperatures were used to give an estimate of realistic temperature effects on glove behavior. Additionally, atrazine was subjected to 55 °C to establish a breakthrough time/temperature relationship. The permeation cell was submerged in the temperature bath with samples extracted at constant time intervals from the collection side of the ASTM cell.

The commercial pesticide mixture is the most concentrated form of the pesticide and therefore represents a worst case exposure to an agricultural worker. Pesticide formulations were used as the challenge solutions. The formulations contain pesticide, surfactant, solvent and fillers that can have an active ingredient (pesticide) content range from 45%-87%.

The solubility parameter segment involved the determination of the 3-dsp of the glove polymer by using several solvents. Methods similar to Perkins' procedures were used to determine the 3-dsp of the glove polymer. The solubility parameter of the polymer and pesticide formulation solvent were used in the discussion of the results. Since the 3-dsp takes variables such as

polarity, dispersion, and hydrogen bonding into consideration in the calculations, it was used for explanation of observed phenomenon rather than the total solubility parameter.

It must be remembered that the pesticide formulation is a complex mixture, which, for proprietary reasons, only limited information about composition is available. These formulations do not contain 100% solvent (as did the challenge solution in other studies). Only a percentage of the mixture is solvent. For this reason, the behavior of the breakthrough times, was expected to differ from previous work in solvent permeation.

Proper safety precautions such as wearing safety glasses and protective gloves were followed at all times.

3.2 PERMEATION

3.2.1 Materials

Solutions

To simulate the actual use conditions of the glove, the pesticide formulation was chosen for the challenge solution and a laboratory perspiration solution for the collection side of the cell. Three pesticides that are representative of popular herbicides and insecticides in current use were used. These were:

Atrazine: a triazine herbicide; 40.8% active ingredient

Diazinon: an organophosphate insecticide; 48% active ingredient

Metolachlor: a chloroactamide herbicide; 86.4% active ingredient

In preliminary tests, the perspiration solution was a standard mixture set by the American Association of Textile Chemists and Colorists (AATCC) in test method 15-1985. It contains :

10 g sodium chloride NaCl

1 g lactic acid USP 85% $CH_3CHOHCOOH$

1 g disodium hydrogen phosphate anhydrous Na_2HPO_4

0.25 g histidine monohydrochloride

The pH was 4.3 ± 0.2.

The solution was made using distilled water to make 1 liter artificial perspiration.

The preliminary testing of the pesticides in the cell revealed that they were possibly unstable in this acidic environment. The diazinon, in particular showed a marked decrease in concentration after 3 hours. Because of this problem, the alternative alkaline perspiration solution from AATCC was used. This solution has a pH of 8.0.

10 g sodium chloride NaCl

4 g ammonium carbonate, USP

1 g disodium hydrogen phosphate, anhydrous Na_2HPO_4

0.25 g histidine monohydrochloride

These ingredients were made up into a 1 liter solution with distilled water.

Samples

Gloves

Two butyl rubber glove styles of differing thicknesses were used for the study. This polymer was chosen because preliminary studies indicated that gloves made from the neoprene polymer, as used in some field situations, showed no breakthrough under 24 hours against the chosen formulations. A 60 mm sample was cut from either the palm or back of the glove hand for testing (flat surface area).

The pertinent physical properties of mass/unit area and thickness of these gloves were measured since these are properties that have been cited as affecting the breakthrough times of challenge solutions. This data was determined by the ASTM standard methods D3776-85 and D1777-64 respectively.

Five samples of each glove polymeric material were cut. Each sample was weighed and measured on five different locations for thickness. The five weights were used to calculate the mass/unit area, and the twenty five thickness measurements were averaged for the thickness value. (Table I)

Table I

Physical Properties of Butyl Glove Material

	Mass/unit	Thickness	
Glove	g/m^2	inches	mil
Thin	324 ± 12	0.0120 ± 0.0007	12.0 ± 0.07
Thick	449 ± 20	0.0176 ± 0.0007	17.6 ± 0.07

Apparatus

The experiments were run in the ASTM permeation cell suspended in a constant temperature bath. A Tracor Gas Chromatograph Model 540 with a flame ionization detector was used. Test parameters:

Inlet temp 230°C

Detector temp 250°C

Column temp 200°C for Atrazine and Diazinon

230°C for Metolachlor

Helium carrier gas: 75 ml/min

Hydrogen gas: 40 ml/min

Compressed air: 250 ml/min

A Spectra physics integrator model SP4290 and the Labnet software package was used to record and store the data.

3.2.2 Procedure

Permeation Testing

The glove sample was clamped between the gaskets of the two sides of the permeation cell with the outside of the glove towards the challenge side. The cell was then

lowered into the constant temperature bath. One hundred milliliters of the perspiration collection solution was pipetted into the collection side then the pesticide was immediately poured through a funnel into the challenge side (about 50 ml). Simultaneously, the timer for the sample withdrawals was started. Throughout the experiment the collection side was stirred vigorously for 2 minutes before sample withdrawal. Two repetitions were performed for a total of three experimental runs for the diazinon and metolachlor. Two replicates were performed for atrazine. Two or three replicates of each test was considered standard procedure as illustrated by the experiments of Perkins (27), Stampher (35), Mickelson (21) and Forsberg (12).

To determine the intervals at which the 100 μl samples should be withdrawn, several preliminary runs were performed. Initially, the cell was run and withdrawn samples analyzed at hourly intervals until two or three successive samples contained active ingredient. This procedure gave the approximate breakthrough time. During subsequent runs of the cell samples were withdrawn every five minutes in the two hour range before and after breakthrough to more accurately fix the breakthrough time.

The withdrawn samples were put into vials of 5 ml of 0.025 M saline solution for refrigerated storage until

they could be extracted (9).

Pesticide Extraction

The withdrawn samples were prepared for analysis by solvent partitioning. Each of the chosen pesticides is soluble in both chloroform and methylene chloride which are insoluble in water. Chloroform was used to extract atrazine. Diazinon and metolachlor were extracted with methylene chloride. The 5 ml saline/pesticide solution was poured into a 60 ml separatory funnel and 5 ml of solvent was added. The vial was rinsed with solvent which was added to the funnel. The funnel was stoppered, shaken with the pressure released intermittently, then let to stand and separate. The bottom layer of solvent was drained from the funnel into the vial. This process was repeated twice. Three extractions gave an efficiency of 85-95% in the preliminary tests.

In these studies, the extract was funnelled through anhydrous sodium sulfate to remove any excess water, but peculiar results suggested that the sodium sulfate might have been holding some of the pesticide. Therefore, subsequent extractions were performed without the sodium sulfate.

In order to condense the extract to a workable concentration that the gas chromatograph (GC) could

detect, the extract was pipetted into a graduated analysis tube. The tube containing the extract was placed into a water bath at the boiling point of the solvent, and the surface of the extract was bathed with nitrogen gas (N_2). The solution was allowed to evaporate to 100-200 μl. It was then pipetted into a 2 ml vial (9).

3.2.3 Analysis

Sample Solution

To analyze the extracted sample for pesticide content, an accurate measurement of the extract was necessary. Using a 1000 μl syringe, the extract was measured and recorded. Four microliters of the extract was withdrawn and then injected into the GC.

The area from the pesticide peak was substituted into the previously determined calibration curve for that pesticide. (Appendix B) From this equation, the concentration of the pesticide was calculated in parts per million (ppm). A correction factor for the amount of the extract solution was added into the calculation to determine the amount of pesticide in the original sample. An example of a typical calculation for a specific 100 μl sample after extraction is:

Calculation 1

Concentration Determination of Sample

Time (min)	Area Peak 1	Vol of sample (μl)	ppm
30	253	90	17.25

The calculation for this data set given the predicting equation of y = 13.2 (x) where y was the area under the peak observed:

$$253 = 13.2\ x$$

$$253/13.2 = x$$

$$17.17\ \text{ppm} = x$$

To correct for the volume of 90 μl when the original sample withdrawn from the cell is 100 μl:

$$17.17\ \text{ppm} \times (90\ \mu\text{l}/100\ \mu\text{l}) = 17.25\ \text{ppm}$$

Therefore, in the original 100 μl sample withdrawn from the cell at 30 minutes, the concentration of the pesticide is 17.25 ppm.

Extraction Efficiency

The extraction efficiency was based on a sample with a known amount of pesticide active ingredient. The sample was extracted in the previously described manner and the amount of the extracted active ingredient was compared to the known amount that should have been extracted. The known amount of pesticide is contained in 10 μl of the formulation. Using the density and percent of active

ingredient, the absolute amount of active ingredient could be calculated. An example of a metolachlor extraction efficiency calculation follows. The metolachlor formulation has 86.4% active ingredient and the density of metolachlor is 1.11 mg/μl (39). Therefore 10 μl of formulation contains:

Calculation 2

Extraction Efficiency

10 μl x 0.864 = 8.64 μl active ingredient

8.64 μl x 1.11 mg/μl = 9.59 mg

There is 9.59 mg of active ingredient in 10 μl of formulation. From the integrator, the concentration of the injected extracted sample can be calculated from the calibration curve. If the concentration is determined to be 17.8×10^3 ppm, to calculate the absolute amount of active ingredient, the volume of the sample has to be measured. In this example the volume is 520 μl.

17.8×10^3 ppm = 17.8×10^3 ng/μl

17.8×10^3 ng/μl x 520 μl = 9.24×10^5 ng

9.24×10^5 ng = 9.24 mg

To determine the efficiency in percent:

9.24 mg/9.59 mg x 100 = 96.0%

This extraction yields a 96% efficiency for this sample.

Four replicates of the extraction efficiencies were performed.

3.3 SOLUBILITY PARAMETER

3.3.1 Materials

The 3-dsp of the glove polymer was determined by using 39 solvents in the 2 dimensional plotting method (26, 27, 28). The 39 solvents have been determined to sufficiently cover the various polarity, dispersion, and hydrogen bonding characteristics to enable an accurate determination of the polymer 3-dsp. (Solvents listed in Appendix C)

3.3.2 Procedure

Perkins' procedure was followed for the experiment. Samples of the rubber, 2 x 2 cm in dimensions were cut and weighed. These samples were each submerged in 10 ml of one of 39 solvents with various parameter values for 14 days. (The solvent list originally had 44 liquids, but it was not possible to obtain some of them.) At the end of this time the samples were plotted and reweighed in a clean, previously weighed vial.

The procedure was repeated 4 times: twice using the thin glove material (12 mil) and twice using the thick glove material (17 mil) (26, 27). The percent weight change for each polymer in solvent was recorded and then

weight gains of 20% or more were plotted on two dimensional graphs (27).

3.4 LIMITATIONS

Because the pesticide active ingredient is a nonvolatile compound, continuous sampling was not feasible. Therefore the discrete sampling was a limiting factor in that the exact time of breakthrough could not be determined. For experiments where the breakthrough occurred under 5 minutes samples were taken from the cell every 1 minute for 5 minutes, otherwise the samples were taken every 5 minutes as previously described.

3.5 DATA TREATMENT

The breakthrough times, by independent variables (temperature, glove thickness and pesticide formulation) was plotted to assess interactions, differences and trends. Where a trend was evident the SAS statistical package was used to analyze the data by means of a least squares regression. This technique indicates the degree to which the data follows a linear pattern that can be attributable to the independent variable.

CHAPTER 4

RESULTS AND DISCUSSION

The results of this study are divided into four major sections. The first part is the extraction efficiency and the problems encountered and solutions developed while achieving acceptable active ingredient extraction. A second section reports the results from the 3-dsp determination of the butyl rubber gloves. The third section addresses the results of the permeation experiments and how the results divide the study into two parts. These two parts are analyzed separately. The fourth part discusses the probable breakthrough mechanisms.

4.1 EXTRACTION EFFICIENCY

The efficiency of the active ingredient extraction is crucial for the determination of the breakthrough time. If the technique is not sensitive enough, then a false breakthrough time might be determined at a time somewhat after the real breakthrough time inaccurately skewing the results. Originally, methylene chloride was to be used as the extraction solvent for diazinon and metolachlor. However, to obtain better efficiencies, other solvents

were evaluated in order to identify a solvent that would provide higher efficiencies of 95% or greater. This efficiency range is markedly better than the 86-95% from the preliminary experiments. (Table II)

Table II

Active Ingredient Extraction Efficiencies

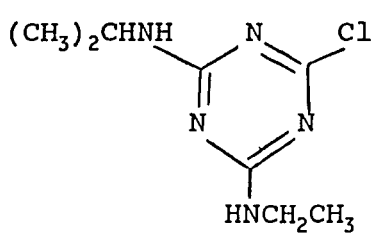
Active Ingredient	Efficiency (%)
Atrazine	91.1 ± 3.9
Diazinon	≈ 99.0
Metolachlor	95.5 ± 0.5

4.1.1 Atrazine

Atrazine is illustrated in Structure **1**.

Structure **1**

Atrazine



Chloroform suggested in the literature as a good solvent for the atrazine, was used in the preliminary testing and yielded an efficiency of 95%. (39) This solvent was kept as the extraction solvent for the remainder of the

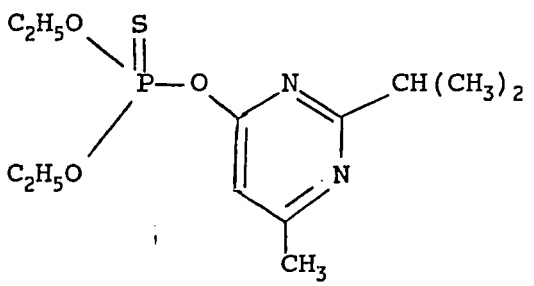
experiments. The efficiency of chloroform is demonstrated by confirming efficiencies that averaged approximately 91%.

4.1.2 Diazinon

Diazinon is presented in Structure 2.

Structure 2

Diazinon



The efficiency of extraction for this active ingredient was approximately 90% with methylene chloride. However, a much better efficiency was achieved with chloroform as the solvent. For three of the replicates, an efficiency of over 100% was obtained. This high efficiency could be due to the method by which the pesticide was measured. Although a 100 μl syringe was used, and 10 μl was carefully measured, there is some room for error. It was possible that the measured amount was slightly more than 10 μl which would contain more active ingredient than the exact 10 μl amount. For this reason, the efficiency is

reported as the lowest amount under 100% obtained from the four replicates: 99%.

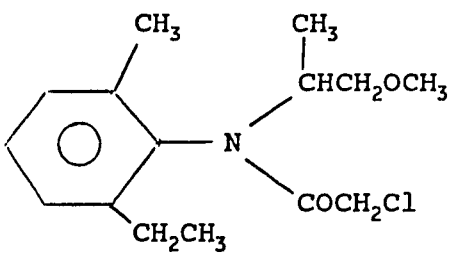
Although efficiencies over 100% were obtained, this can be interpreted as support for a very high extraction efficiency with this solvent. The high pesticide ingredient level in the extract demonstrates the extraction efficiency of chloroform.

4.1.3 Metolachlor

Metolachlor is illustrated in Structure 3.

Structure 3

Metolachlor



Metolachlor also was originally to be extracted with methylene chloride and because this solvent yields an efficiency of 86%, it was to remain the extraction solvent. However, when the efficiencies were performed again in replicates, the concentrations of the samples were inconsistent and the efficiency was no more than 44%. This value was significantly lower than the values

obtained in the preliminary extraction tests. Because of these erratic results, another solvent system had to be explored.

Chloroform was considered as an alternative solvent but because it is so close to methylene chloride chemically, it was doubtful that it would yield an efficiency significantly closer to 100%. Because metolachlor is slightly more soluble in water than either atrazine or diazinon, a more polar solvent was needed to pull the metolachlor out of the water. A combination of polar solvent, that would pull out the water soluble metolachlor, and solvent that would extract the non-solubilized active ingredient, was tested. The more polar solvent ethyl acetate was tried for two and chloroform for the third extraction of each sample. This combination gave an efficiency over 95%. Again, two of the replicates had an efficiency over 100%. Therefore, the reported efficiency only includes the efficiencies under 100%: 95.5%. These efficiencies are high enough so a relatively accurate breakthrough time can be determined from the discrete samples.

4.2 SOLUBILITY PARAMETER

There are several ways to determine the solubility parameters of a polymer. The calculation method uses group molar attraction constants to determine the

solubility parameters. Each group from the monomer structure contributes an amount of energy to the intermolecular cohesion energy. These values can be found in reference tables (2, 37).

The experimental method is based on the degree of swelling of the polymer in a series of solvents with known parameters. The polymer will swell appreciably in solvents that have the same or similar parameters. From the swelling behavior, the polymer solubility parameters can be approximated from those of the solvents. To determine the values of the Hansen 3-dsp solubility parameters for the vulcanized butyl rubber used in this study, both calculation and experimental methods were used.

4.2.1 Solvent Series

To experimentally determine the 3-dsp, three graphs were used to plot the parameters of the solvents. These graphs plot dispersion against polarity; polarity against hydrogen bonding; and dispersion against hydrogen bonding of the solvents. The solvents that yielded a 20% or more weight gain are indicated on the graphs. A circle was drawn around the solvents so the coordinate points of the circle center could be determined. These coordinates were averaged for the final estimate of that parameter component. Although the thick polymer glove material

exhibited greater absolute weight gain, the percent weight gains were comparable between the thin and thick glove materials. This similarity indicates that the thickness is not a factor in characterizing solubility. Figures 1, 2 and 3 show the plots of the > 20% weight gain. The center of the circle was placed near the cluster of solvents that displayed consistent weight gain in 3 and 4 replicates. (Figures 1, 2, 3)

From the graphs, the 3-dsp for the butyl rubber was determined to be:

Calculation 3

3-dsp from Solvent Experimentation

$$\delta_d = (18.1 + 18.5)/2 = 18.3 \ (J/cc)^{1/2}$$

$$\delta_p = (1.5 + 2)/2 = 1.75 \ (J/cc)^{1/2}$$

$$\delta_h = (2.0 + 3.9)/2 = 2.9 \ (J/cc)^{1/2}$$

Using these figures, the total solubility parameter was calculated using Equation 4:

$$\delta_t = [(18.3)^2 + (1.75)^2 + (2.9)^2]^{1/2}$$

$$\delta_t = 18.6 \ (J/cc)^{1/2}$$

4.2.2 Calculations from monomer groups

Butyl rubber is the copolymer of isobutylene and isoprene. Because the isoprene is randomly present, a representative structure was obtained from an organic

Figure 1 3-Dimensional Solubility Parameter

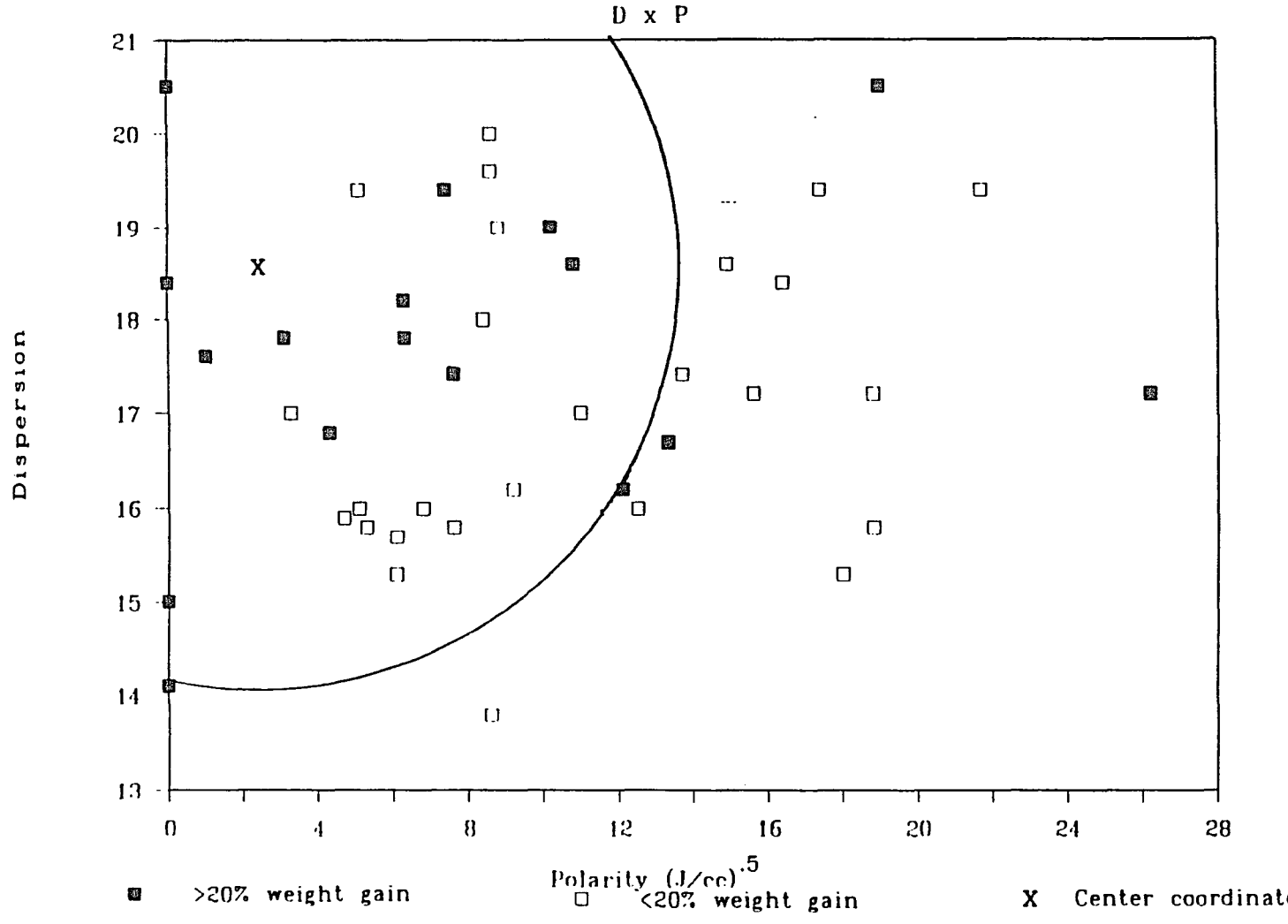


Figure 2 3-Dimensional Solubility Parameter

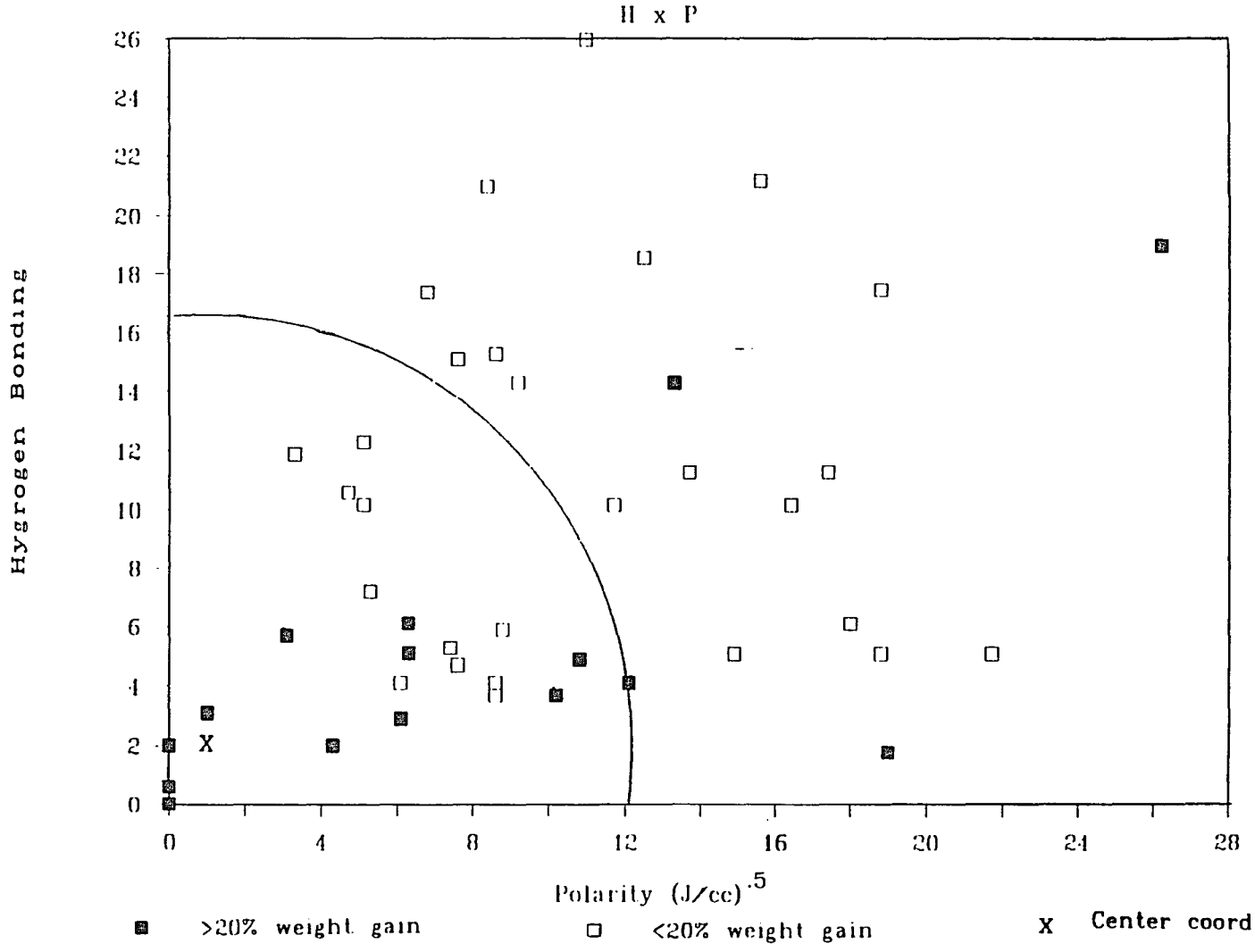
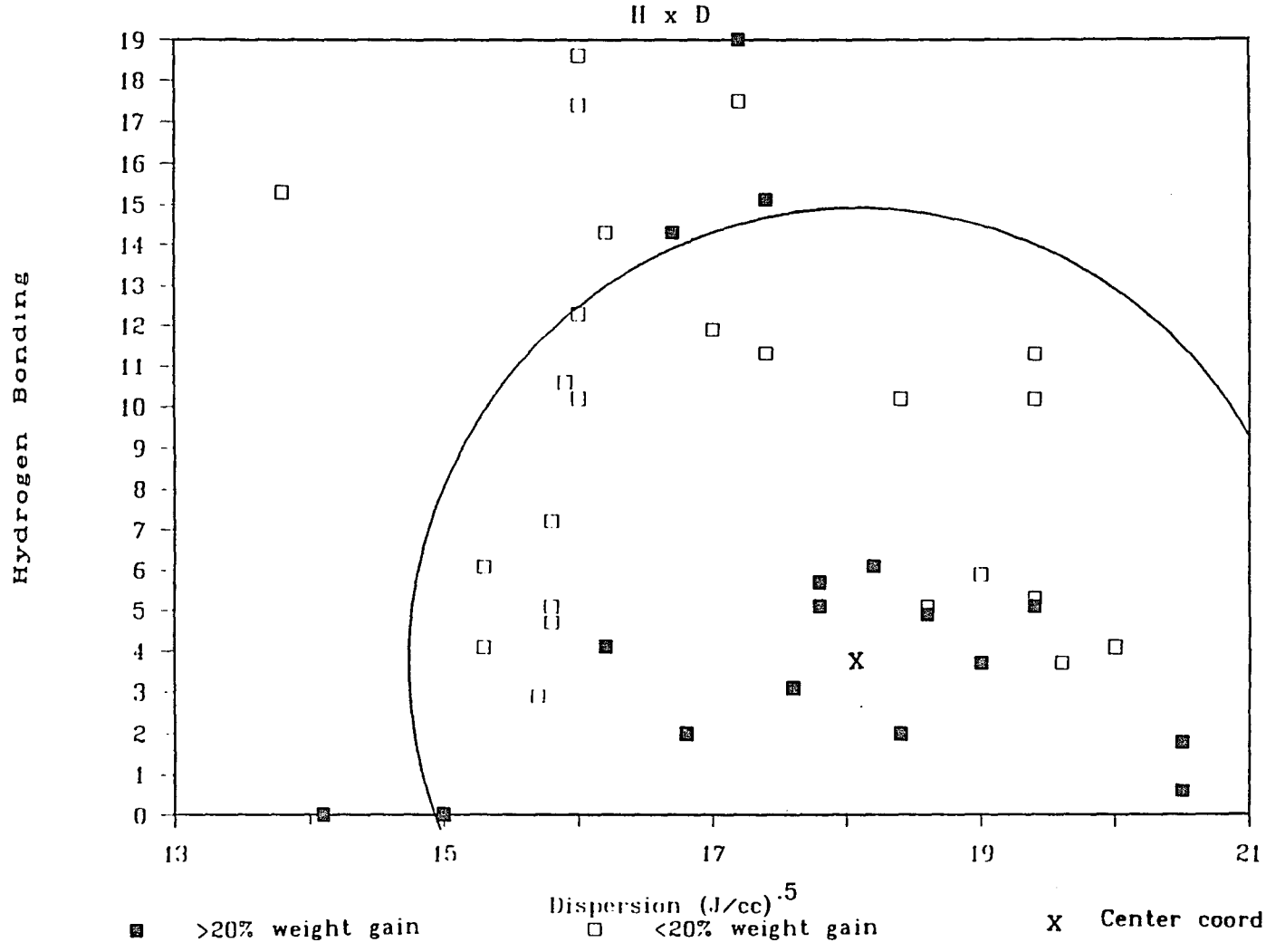


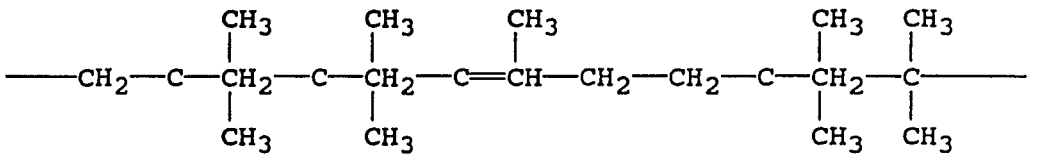
Figure 3 3-Dimensional Solubility Parameter



polymer book and was used as the structure from which to calculate the values (31). (Structure 4)

Structure 4

Random Monomer Structure of Butyl Rubber



The molecular weight of the butyl rubber segment is 292 g/mole and the density of vulcanized butyl rubber is 1.13 g/cc (8) which means that the molar volume is calculated to be 258. To determine the individual components, the formulas for dispersion (Equation 1) and hydrogen bonding (Equation 2) were used. Table III displays the dispersion molar attraction constants for the pertinent groups of the rubber structure. Calculation 4 determines the dispersion force from the copolymer structure. The hydrogen bonding parameter was estimated in the same manner using the cohesive energy for the functional groups. (Table IV)

Calculation 4

Dispersion Force

$$\delta_d = 5390/258 = 20.9 \ (J/cc)^{1/2}$$

Table III

Dispersion Group Molar Attraction Constants

Group	n	$F_d/J^{1/2}$ cm $^{3/2}$ mol $^{-1}$	Total
$-CH_3$	9	420	3780
$-CH_2-$	6	270	1620
$-C<$	4	-70	-280
$>C=$	1	70	70
$=CH-$	1	200	200
			5390 (37)

Table IV

Cohesive Energy of Groups

Group	n	$-U_h/J$ mol $^{-1}$	Total
$-CH_3$	9	0	0
$-CH_2-$	6	0	0
$-C<$	4	0	0
$>C=$	1	0	0
$=CH-$	1	0	0
			0 (37)

$$\delta_h = \sqrt{(0/258)} = 0 \text{ (J/cc)}^{1/2}$$

Generally, the polarity portion of the total parameter is approximated by the correlations from dipole moments of liquids. Hydrocarbons with structure similar to butyl rubber do not normally have permanent dipole forces. The values listed for these groups are all 0 also. Therefore the parameter value for polarity is zero. From Equation 4 the total solubility parameter is calculated to be:

Calculation 5

Calculated Total Parameter from Functional Groups

$$(20.9)^2 = (0)^2 + (0)^2 + x^2$$

$$x = 20.9 \ (J/cc)^{1/2}$$

Table V has been constructed to summarize the data. Another experimentally determined 3-dsp of butyl rubber was obtained from the CRC reference for solubility parameter and added to the table for comparison purposes.

Table V

Data Summary

Component	Experiment	Calculated	CRC
dispersion	18.3	20.9	16.0
hydrogen bonding	2.9	0	3.3
polarity	1.8	0	2.3
total	18.6	20.9	16.5

The calculated and experimentally determined values are very similar in the dispersion and total parameters, but seem somewhat far apart in the polarity and hydrogen bonding components. The calculated value might be higher than the other value because butyl rubber is polymerized in a random arrangement of the two monomers rather than in uniform units containing a prescribed amount of both monomers. A random structure was used as the basis of the calculated parameters.

Additionally, the values for the calculated and CRC polarity and hydrogen bonding parameters are not very close (2). However the values for the CRC and the experimentally determined polarity and hydrogen bonding parameters are close.

Although the dispersion figures look different from the CRC value of 16.0 they are within the polymer swelling range (2). (Table VI) The CRC gives the ranges of swelling for the isobutylene-isoprene copolymer as:

Table VI

25% swell range J/cc $^{1/2}$

δ_d	δ_p	δ_h
13.7/20.9	0.0/6.3	0.0/7.4

Even though these ranges are for 25% swelling, and the experimental data was taken at 20%, the experimental

ranges of swelling are within the reference ranges as shown in Figures 1, 2 and 3.

A hydrocarbon structure would theoretically have only a dispersion force. This single force could be the reason why the 3-dsp values from strict calculation only give a value for this component. However, values were obtained experimentally for polarity and hydrogen bonding. Therefore other factors which would explain the values observed for the polarity and hydrogen bonding components must be involved. The butyl rubber used in the experiments is milled for a specific end-use, so additives such as carbon black, lubricant (zinc stearate) and antioxidant (phenyl ß-naphthylamine) might account for some of the variation and the interaction of the solvent with the polymer in the polarity and hydrogen bonding dimensions.

Because the swell ranges match well, it was concluded that the experimental and calculated solubility parameter components were a feasible approximation of the parameters. However, because these parameters were an integral part in this breakthrough study, they were experimentally determined for this specific material to detect any possible change in solubility components due to additives.

4.3 BREAKTHROUGH TIME

When working with the permeation cell, great care had to be taken to prevent cross-contamination which would bias the results. Three problems can occur which would alter results of the breakthrough time. If the prepared volume of the sample is too much over the original 100 μl then the detection of the breakthrough time might be delayed. If the glassware that is not expendable, such as the graduated analysis tubes and separatory funnels, are not scrupulously cleaned after each use, then cross-contamination may occur that could result in a false early breakthrough time and detection of higher concentrations of active ingredient.

Although the absolute amount of active ingredient was not used for permeation rate analysis, it was used as a method of validation for the experiments. If about the same concentration was detected at about the same breakthrough time of each replicate then the breakthrough was assumed to be valid.

One problem was unique to the metolachlor. Because the preliminary extraction efficiency was 86%, the confirming replicates were not performed until some of the permeation experiments had been executed. When the efficiency was repeated with dismal figures of 44%, the results from the metolachlor experiments were deemed

invalid. Those experiments were repeated after a suitable solvent system had been found for the extraction.

For these three reasons, some of the experiments had to be repeated more than three times to obtain consistent results from replicate to replicate. After the problems were resolved, data collection began. Three replicates were averaged to determine the metolachlor and diazinon breakthrough time. However, because the atrazine breakthrough times were so consistent and distinctly different between temperatures and from the other two formulations, it was decided that only two replicates were appropriate. Table VII presents the raw data and Table VIII the means and standard deviations of the breakthrough times.

The results are better illustrated by plotting the average breakthrough times. Figure 4 illustrates the three-way interaction of the independent variables pesticide, temperature and glove thickness. For both the thin and thick gloves the means of metolachlor and diazinon are similarly low which results in the lines overlapping near the floor of the graph. Means for the thin and thick gloves subjected to the atrazine formulation are very different from the other two formulations and suggest, from the sloped lines, that

Table VII

Raw Data Breakthrough Time (min) at 35°C and 45°C

	Temperature					
Glove Thickness	35°C			45°C		
	Replicates					
Diazinon	1	2	3	1	2	3
12 mil (Thin)	1	1	2	1	2	1
17 mil (Thick)	1	1	1	1	1	2
Metolachlor						
12 mil (Thin)	1	4	4	1	2	1
17 mil (Thick)	1	1	4	1	2	3

	Replicates			
Atrazine	1	2	1	2
12 mil (Thin)	1250	1245	55	65
17 mil (Thick)	3630	3660	2460	2475

Table VIII

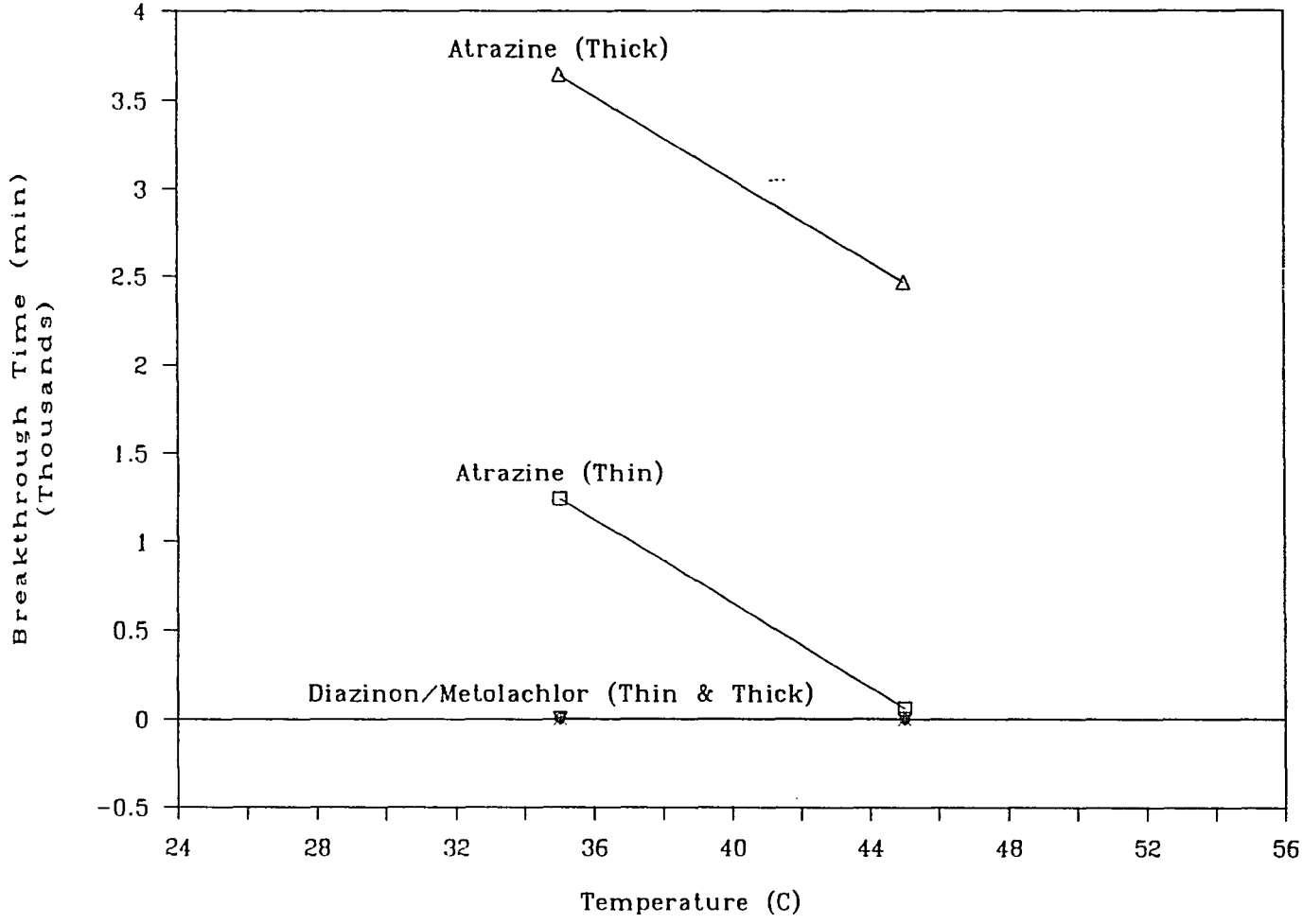
Breakthrough Time (min) of Pesticide Formulations at 35°C and 45°C

Glove Thickness	(n)	Temperature 35°C	45°C
		Diazinon	
12 mil (Thin)	3	1.3 ± 0.6	1.3 ± 0.6
17 mil (Thick)	3	≤ 1.0	1.3 ± 0.6
		Metolachlor	
12 mil (Thin)	3	3.0 ± 1.7	1.3 ± 0.6
17 mil (Thick)	3	2.0 ± 1.7	2.0 ± 1.0
		Atrazine	
12 mil (Thin)	2	1247.5 ± 3.5	60.0 ± 7.1
17 mil (Thick)	2	3645 ± 21.2	2467.5 ± 10.6

there is an interaction due to pesticide formulation. However, the relationship between the pesticides within the grouping of the thin versus thick glove is the same. The atrazine lines for the two glove types are parallel to each other and interact similarly with the lines representing diazinon and metolachlor. This suggests that there is not a three-way interaction where the effect of temperature depends upon both the level of glove thickness and pesticide formulation. To further investigate the factors that affect the breakthrough time

Figure 4

Three-Way Variable Interaction



plots with two variables were constructed.

Figures 5 and 6 show the two-way relationships between the breakthrough times of the pesticides and the temperature and glove thickness respectively. As expected, metolachlor and diazinon have virtually the same horizontal line along the floor of the graph. The atrazine, in both cases, has a decided sloping line. These plots indicate that the effect of temperature and glove thickness depended upon the type of pesticide formulation. A third plot (Figure 7) illustrates the effect of temperature and glove thickness on breakthrough time. The parallel lines suggest that the effect of temperature did not depend on the thickness of the glove. The higher temperature yielded a lower breakthrough time that was proportional between glove thicknesses.

Additionally, the overall mean of each independent variable category has been tabulated in Table IX. The means within each variable look very different. However, because two two-variable interactions have been determined as discussed above, the categorical means can not indicate any specific effect due solely to a particular independent variable.

Relationship Between Breakthrough Time

and Independent Variables

Figure 5

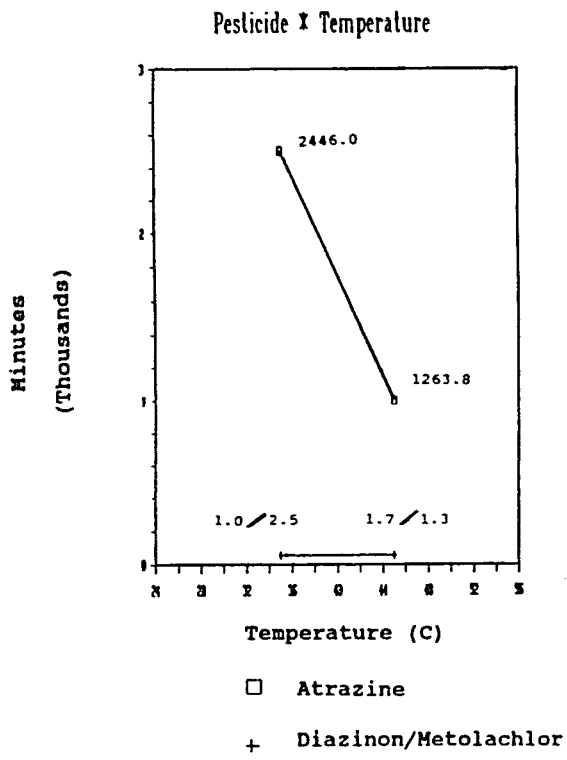


Figure 6

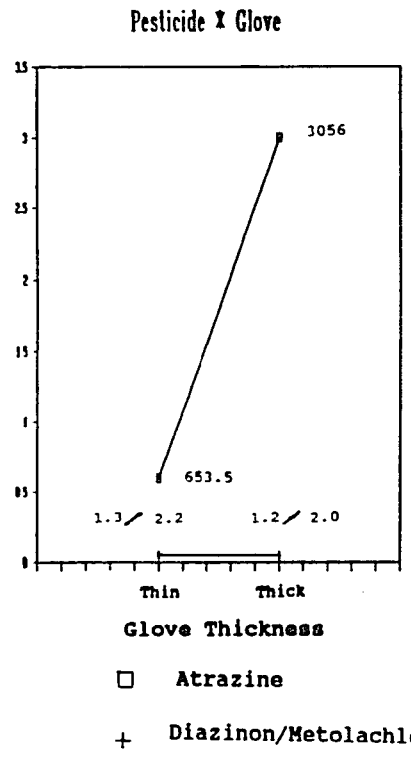


Figure 7

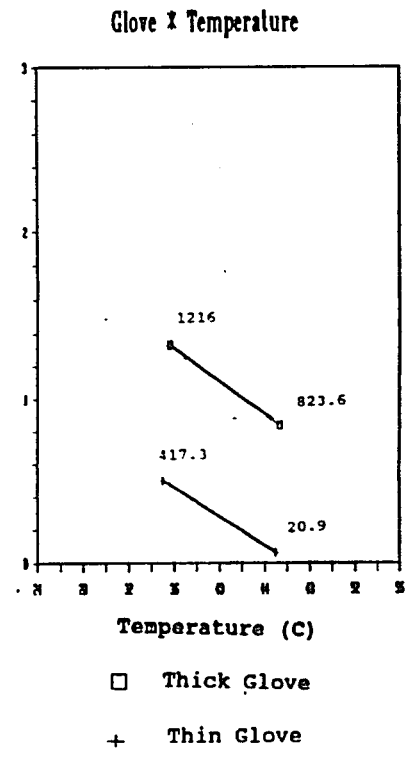


Table IX

Main Effects Means

Independent Variable	Breakthrough Time (min)
Temperature	
35°C	650.0
45°C	422.2
Glove Thickness	
Thin	218.7
Thick	1020.0
Pesticide	
Atrazine	1855.0
Diazinon	1.2
Metolachlor	2.3

It was at this point that the study lent itself to two separate parts because two pesticides behaved similarly but differently from the third pesticide. The diazinon and metolachlor data was treated as one section and the atrazine another. The breakthrough times between 35°C and 45°C did not seem appreciably different for diazinon and metolachlor. The atrazine, however, showed a much different breakthrough behavior. Because this formulation exhibited a pattern of longer and very consistent breakthrough times, it was decided to continue with two replicates and expand the temperature conditions

from two to at least three temperatures for the purpose of determining a pattern of dependence.

4.3.1 Diazinon and Metolachlor

From Table VIII, the breakthrough times of the diazinon and metolachlor are virtually the same from temperature to temperature and glove thickness to glove thickness. Looking only at glove thickness between pesticides, an average breakthrough of about 1.2 minutes for the diazinon through the thick is not very different from 2.0 minutes for metolachlor through the same glove thickness. Additionally, the behavior of the thin glove mimics the thick. Diazinon has a breakthrough time of approximately 1.3 minutes compared to metolachlor 2.2 for the thin glove.

Temperature alone also did not seem to play a large role in the breakthrough of these two formulations. At the higher temperature the diazinon breakthrough was approximately 1.3 minutes and the metolachlor 1.7 minutes. At the lower temperature, there was more of a difference between the two (≈ 1.0 and 2.5 minutes respectively) but this difference is not practically significant.

It was apparent that there is something or some things common to these two formulations that caused similar breakthrough behavior. This behavior could have

been caused by ingredients common to both of the formulations such as solvent or surfactant.

4.3.2 Atrazine

The longer breakthrough times of the atrazine formulation suggested that a different mechanism, from the previous two pesticides, was responsible for the breakthrough behavior. This mechanism could be diffusion. The diffusion would be driven by the concentration gradients across the barrier. As the components of each side of the cell cross the barrier on a molecular level, the chemical potential moves from high to low energy or toward equilibrium. In infinite time, the concentration of each component will be the same on both sides of the glove barrier. In this respect, the atrazine formulation was believed to follow Fick's law of diffusion. If a diffusion mechanism was present, perhaps a temperature dependence also existed.

The breakthrough times exhibited at 35°C and 45°C seemed to be temperature dependent. One way of illustrating temperature dependence would be by adapting the Arrhenius equation to the situation. The Arrhenius relationship is a temperature dependence of rate constants and activation energy of a reaction. According to the Arrhenius theory, the rate constant is determined by the ratio of the activation energy to the temperature and by

the frequency of collision of molecules that produce a reaction. Arrhenius' equation is:

$$k = A \exp (-E_A/RT)$$

where k = rate
A = frequency of molecular collisions
E_A = activation energy
R = gas constant
T = temperature in degrees Kelvin

For any reaction that obeys this equation, a plot of ln k against 1/T will be linear, with slope $-E_A/R$.

This theory may be applied to this experiment by studying the temperature dependence of the breakthrough times. It was assumed the rate difference depends upon the concentration of pesticide in the formulation making the diffusion a first-order process. If this assumption is valid, then the rate would be proportional to changes in concentration and the inverse of changes in time as shown in the following rate expression:

$$dx/dt = k$$

where x = concentration
t = time

Therefore instead of plotting the natural log of the rate, the natural log of the inverse breakthrough time was used. If the Arrhenius relationship holds for this system, then the activation energy of diffusion can be calculated from the slope of the plotted data.

In order to test this idea the thin and thick butyl gloves were subjected to the atrazine formulation under the higher temperature of 55°C. The standard laboratory temperature of 25°C was not chosen because the projected breakthrough time would have been excessively long. For the thin glove an additional temperature (50°C) was also used because the plot of the points deviated slightly from a linear trend. The thick glove had a linear trend after plotting the 55°C point therefore the additional temperature was not used. The data points for the atrazine under all temperatures is presented in Table X.

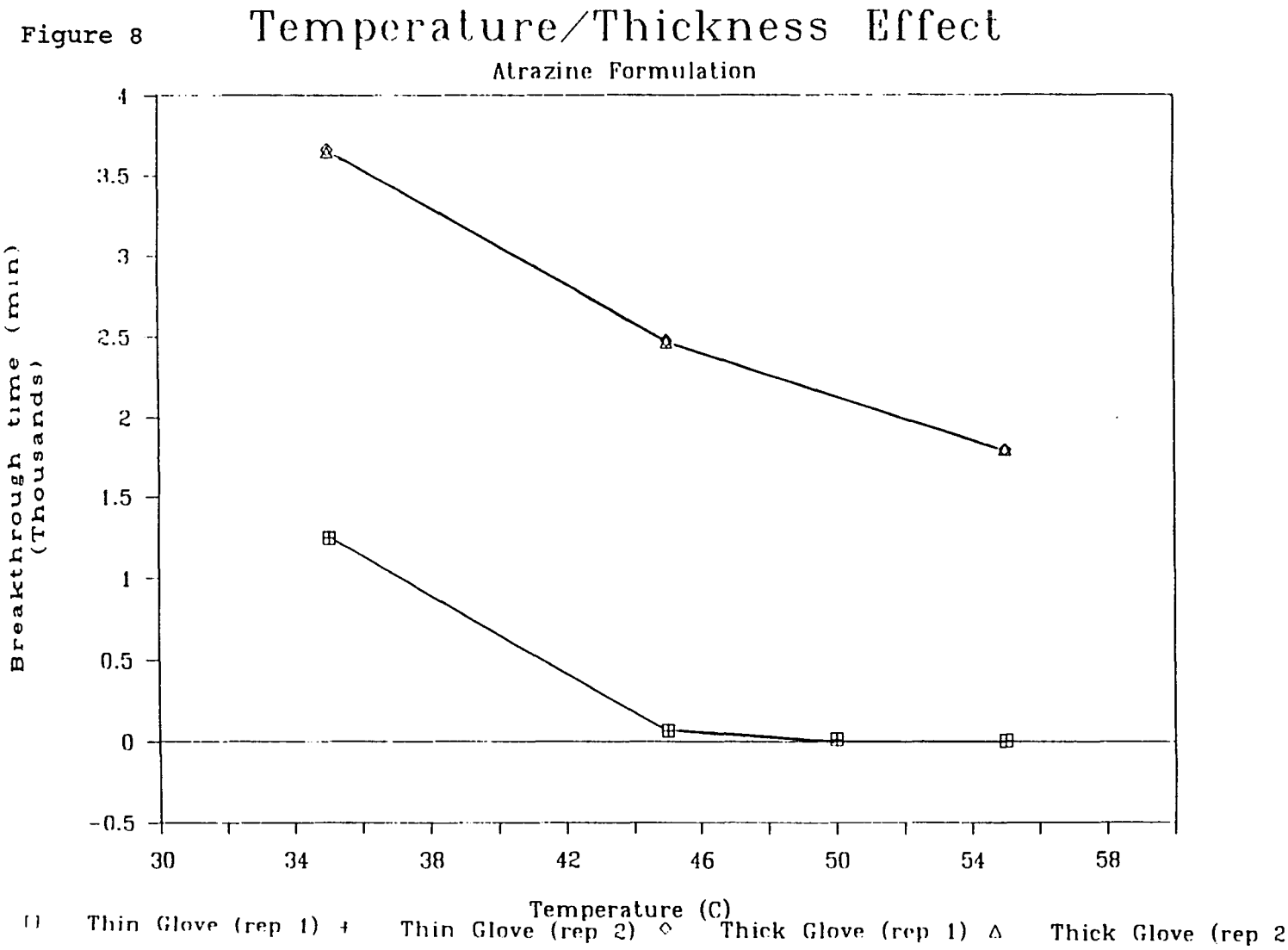
Table X

Breakthrough Time of Atrazine Active Ingredient

Glove Thickness	Temperature			
	35°C	45°C	50°C	55°C
Thin	1247.5 ± 3.5	60.0 ± 7.1	10.0 ± 0	2.0 ± 0
Thick	3645 ± 21.2	2467.5 ± 10.6	-	1800 ± 5.0

Temperature increase had the effect of lowering the breakthrough time and revealing a difference between the thin and thick glove materials. Figure 8 which illustrates the effect of the thin and thick glove material refutes the conclusion drawn from Figure 7 that there is no interaction between temperature and glove

Figure 8


Temperature/Thickness Effect
Atrazine Formulation
Breakthrough time (min)
(Thousands)
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
30
34
38
42
46
50
54
58
Temperature (C)
Thin Glove (rep 1)
Thin Glove (rep 2)
Thick Glove (rep 1)
Thick Glove (rep 2)

thickness. (Figure 7) Figure 7 was plotted with only two temperatures and included the average of all three pesticide formulations. When the diazinon and metolachlor effects were removed, and other temperatures used, it became apparent that the effect of the temperature did depend on the level of glove thickness.

Between the temperatures of 35°C and 45°C the time difference between the two materials remained approximately 1200 minutes (20 hours). When the temperatures were increased to 55°C the thin glove was affected more. The breakthrough time for this glove, at 55°C, dropped to 2 minutes. This drop was a decrease of 99.8% from the time at 35°C and 96.7% from 45°C. The thick glove displayed a drop of 50.6% and 27.1% from these two temperatures respectively. The difference between the two formulation breakthrough times at 55°C was 1800 minutes (30 hours). It was apparent that temperature affected the breakthrough time of the thick glove material less proportionately than the thin. As the thickness increased, the effect of temperature became less important in the breakthrough time behavior.

Arrhenius relationship plots of the data in Figures 9 and 10 show a linear trend. A least squares linear regression performed on the means of the two data plots yielded an R^2 of 0.997 and 0.998 for the thin and thick

Figure 9

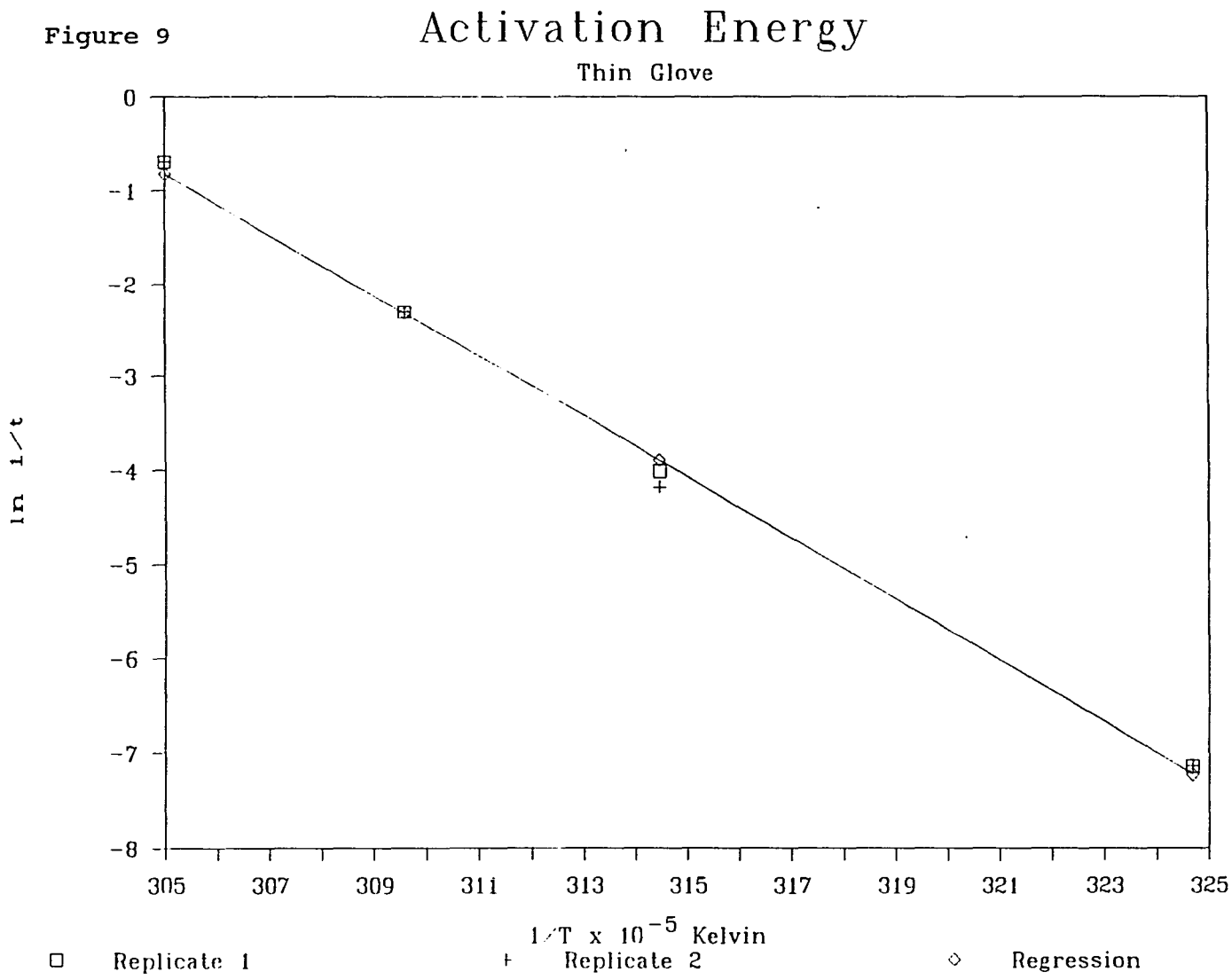
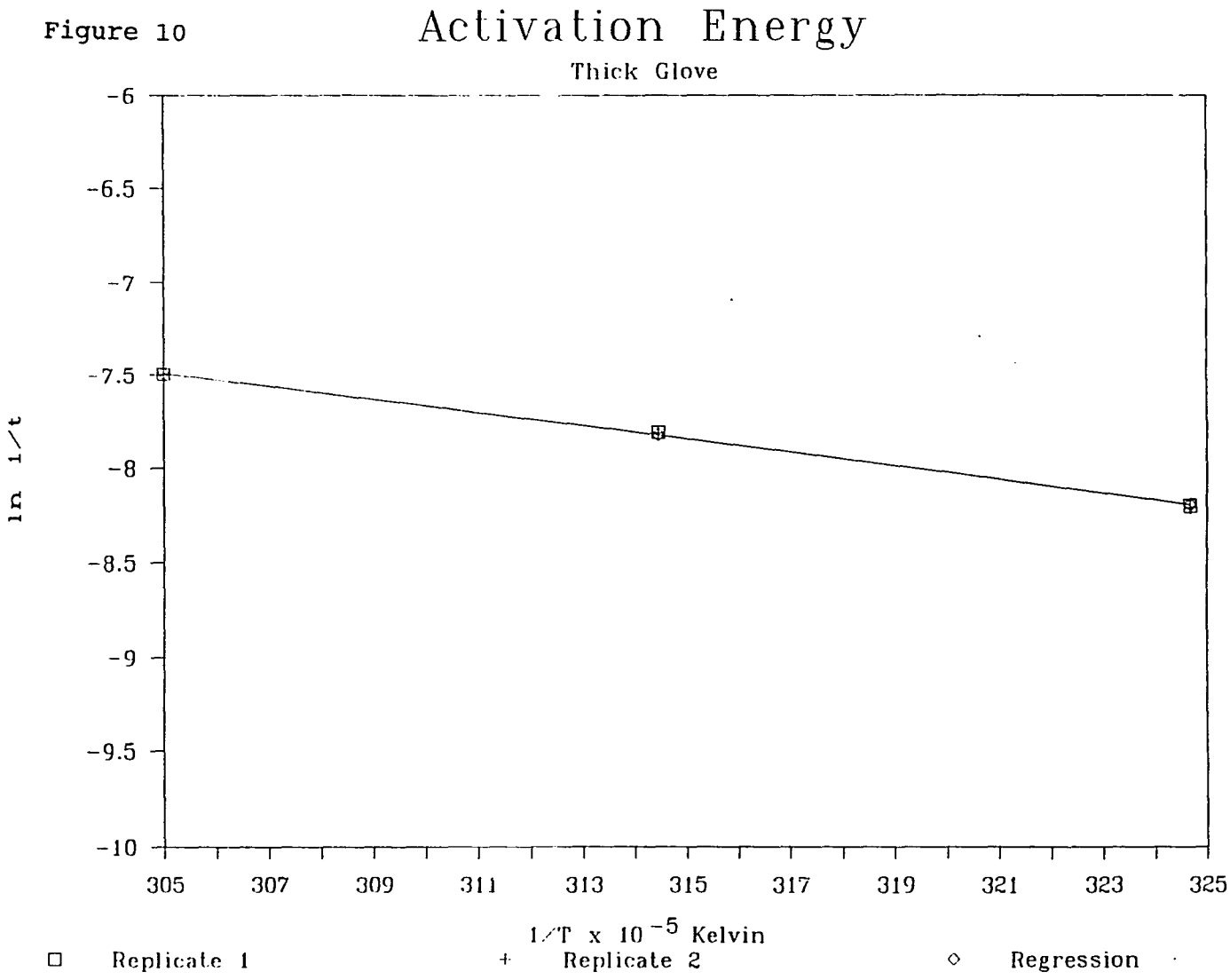

Activation Energy
Thin Glove
0
-1
-2
-3
-4
-5
-6
-7
-8
ln 1/t
305
307
309
311
313
315
317
319
321
323
325
1/T x 10^-5 Kelvin
Replicate 1
Replicate 2
Regression

Figure 10


Activation Energy
Thick Glove
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
ln 1/t
305
307
309
311
313
315
317
319
321
323
325
1/T x 10 -5 Kelvin
Replicate 1
Replicate 2
Regression

glove respectively. The graphs also indicated that the slope of the thin glove is much steeper than the thick glove. Although this difference in slope is not logical intuitively, this steeper slope for the thin glove indicates that the activation energy would be greater for the thin than thick glove. The lesser slope for the thick glove indicates that temperature had a marginal effect on the breakthrough time when the physical barrier of thickness is increased a sufficient amount (5 mil, in this case).

From these plots the activation energy of the atrazine diffusion can be calculated.

Calculation 6

Calculation of Activation Energy of Diffusion

Thin Glove:

From the regression equation y = 32508.9x - 98.33, the slope is 32508.9; gas constant = 8.314 J K^{-1} mol^{-1}.

$$\text{slope} = -E_A/R$$

$$-3.251 \times 10^4 = -E_A/8.314 \text{ J } K^{-1} \text{ mol}^{-1}$$

$$-3.251 \times 10^4/8.314 \text{ J } K^{-1} \text{ mol}^{-1} = -E_A$$

$$2.703 \times 10^5 \text{ J mol}^{-1} = E_A$$

Thick Glove:

From the regression equation y = 3566.15x - 3.39, the slope is 3566.15; gas constant = 8.314 J K^{-1} mol^{-1}.

$$\text{slope} = -E_A/R$$

$$-3.566 \times 10^3 = E_A/8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$-3.566 \times 10^3/8.314 \text{ J K}^{-1} \text{ mol}^{-1} = -E_A$$

$$2.965 \times 10^4 \text{ J mol}^{-1} = E_A$$

From these two calculations the amount of energy needed to diffuse this atrazine formulation through the thin polymer was 2.703×10^5 J mol^{-1}; through the thick polymer 2.965×10^4 J mol^{-1}. The expectation of a greater diffusion activation energy for the thin glove than the thick glove was correct. This difference indicates that the energy calculation for the thick glove was not necessarily accurate because the thickness of the barrier played an important role in altering the breakthrough time pattern. The thicker glove had a greater mass per unit area. This mass may have been enough to alter the diffusion behavior under various temperature conditions.

The thin glove was more affected by the temperature changes hence the activation energy is probably a reasonable estimate by comparison. This system behaved in a manner consistent with the law of diffusion and temperature dependence.

4.4 BREAKTHROUGH MECHANISMS

It was clear from the two parts of this study that there were two general mechanisms involved that influenced

the breakthrough times of the different pesticide formulations. One phenomenon was a solvent/polymer interaction, and the other was a temperature/formulation interaction.

In the solvent/polymer interaction, there are two subcategories: solvent degradation of the polymer molecule or cross-links and Fickian diffusion. To determine if the solvent was chemically interacting with the glove polymer, it was necessary to determine the solvent used in each of the pesticide formulations. Diazinon and metolachlor contained xylene, but the atrazine contained ethylene glycol. An indication of a connection between the breakthrough behavior and the solvent characteristics of the formulations was apparent. The diazinon and metolachlor contained the same solvent and behaved similarly against the butyl glove while the atrazine contained a different solvent and had a different breakthrough pattern.

Table XI suggests one possible reason for breakthrough behavior. The 3-dsp of the xylene and butyl rubber match well. This similarity suggested that the solvent and polymer molecules had similar enough intermolecular forces that the probability of a solvent molecule combining with a polymer molecule was as

favorable as a solvent/solvent or polymer/polymer attraction.

For this reason, it was believed that this chemical interaction was responsible for the almost immediate breakthrough times of the diazinon and metolachlor formulations. The solvent degraded the polymer intermolecular order which allowed the active ingredient to pass into the collection side of the permeation cell. This degradation was the most influential factor in this breakthrough mechanism.

Table XI

Solvent/Polymer Interaction

3 Dimensional Solubility Parameter

$J/cc^{1/2}$	Butyl Rubber	Xylene	Ethylene Glycol
Dispersion	18.3	17.6	17.0
Polarity	1.7	1.0	11.0
Hydrogen Bonding	2.9	3.1	26.0
Total	18.6	17.9	33.0

Conversely, the parameters of the ethylene glycol and the butyl rubber are dissimilar. Although the two dispersion values are similar, dispersion is the weakest attraction force. The other two solubility components (polarity and hydrogen bonding) are markedly different. For this reason the major factor driving the atrazine

breakthrough pattern was attributed to something other than like solubility parameters.

Because of the poor match between the ethylene glycol and butyl rubber, the earlier premise of Fickian diffusion was supported. There seemed to be an absence of a major effect credited to the solvent on the breakthrough time of the active ingredient.

Temperature, nevertheless, played an important role in diffusion where it did not in the degradative solvent/polymer interactions. The various elevated temperature conditions increased the kinetic energy of the challenge solution and the polymer thereby lowering the breakthrough time. Thickness of the material altered the diffusion response to temperature by means of a physical barrier. This barrier, when sufficiently increased, becomes an independent variable which can alter the breakthrough time of the active ingredient under similar temperature conditions.

CHAPTER 5

CONCLUSION

The stated objectives of this study are to determine the breakthrough time of three pesticides, and to study the effects of the pesticide formulations, temperature increase, and glove thickness on the breakthrough time. The results from these experiments suggest that there are two major mechanisms that contribute to the breakthrough time: solubility and diffusion. Depending upon which mechanism dominated the system, the breakthrough time will be differently affected by the independent variables temperature, glove thickness and pesticide formulation.

5.1 SOLUBILITY

When there is a chemical interaction between the glove polymer and solvent carrier in the pesticide formulation, this interaction takes precedence over other variables. Neither differing glove thickness of the commercially available gloves, type of pesticide active ingredient, nor temperature change affects the breakthrough times. For practical application these breakthrough times are instantaneous (1-4 minutes). This degradative interaction occurs when the intermolecular cohesion parameters match.

A common bond between the two formulations (diazinon and metolachlor) was the solvent carrier in the mix. Both contained xylene which had similar solubility parameters as those for butyl rubber. The additional fact that the percent of xylene in the diazinon and metolachlor solutions differ (≈ 52% and ≈ 14% respectively) supported this conclusion that the chemical interaction was the major reason for breakthrough behavior rather than other factors.

5.2 DIFFUSION

When a degradative explanation is not primary, then the mechanism of breakthrough is diffusion caused by the concentration differences on either side of the polymer barrier. This diffusion is affected by temperature increases and glove thickness. A conclusion regarding the effect of different pesticide formulations can not be reached in this study because only one formulation exhibits diffusion behavior.

When the temperature is raised, the breakthrough time decreases. The increased kinetic energy of the polymer and pesticide formulations probably contributes to the lowered breakthrough time. This effect of temperature follows an Arrhenius relationship in that the natural log of the reciprocal breakthrough time is linear when plotted against the reciprocal of the temperature. The slope of

this plot can then be used to calculate the activation energy of the diffusion process.

Glove thickness affects the diffusion mechanism by increasing the breakthrough time, and decreasing the activation energy. Lengthened breakthrough time is due to the increase in the physical barrier and hence, the mass and length through which the active ingredient has to travel. These properties also are responsible for the decrease in the importance of the activation energy. An increase in the glove barrier acts as an insulator so that the effect of a temperature increase is minimized.

The two factors of temperature and glove thickness do not act independently of one another but interact. The breakthrough time of the active ingredient depends upon the temperature and glove thickness.

5.3 PROTECTIVE GLOVE SELECTION

Determination of the absolute breakthrough times of these pesticide formulations is useful for future reference. This data could be accessed through a protective clothing data base. The general benefits of this study though are to suggest some guidelines that can be implemented in the agricultural community to make glove selection more efficient.

1. Minimize positive solvent/polymer interaction.

To maximize protective glove performance, cooperation is needed from the manufacturers of pesticide formulations and protective gloves. One helpful step would be for the manufacturers of pesticides to publish the solvent carrier in the formulation on the label. Additionally, if glove manufacturers provide charts that outline the polymer solubility parameters and parameters of reagent solvents, then these numbers could easily be compared to make an intelligent protective glove selection.

2. Minimize temperature effect.

Once a glove has been selected for the pesticide formulation, then a slightly thicker glove may minimize the effect of working condition temperatures based on these results.

Use of these guidelines could eliminate considerable preliminary costly and time consuming testing.

CHAPTER 6

RECOMMENDATIONS

To further the understanding of factors that affect the breakthrough time in diffusion, experiments that isolate different components of the formulations should be conducted. This study had to be somewhat qualitative because the actual percentages and identification of the formulation ingredients is proprietary information. If this information were accessible it might be possible to isolate substances in the mixture which affect the breakthrough time more exactly.

One suggestion would be to create laboratory pesticide formulations. These formulations could be designed with specific ingredients at known concentrations. The study could be designed so the effects due to specific ingredients could be isolated. The comparisons of the results would better illuminate the roles of the surfactant, active ingredient, molecular size, and percent of ingredients of the formulations play in the level of protection provided by gloves.

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APPENDIX A

GLOVE SELECTION GUIDELINES

These guidelines for glove selection appeared in the June 1988 issue of Safety and Health (29) which is published by the National Safety Council. This is the only published list of official rules which guide selection and use of gloves.

National Safety Council Guidelines

Preliminary Information Before Glove Selection

1. Review processes, work practices and engineering controls for ways to eliminate the need for gloves. Glove use should be the last approach considered to provide employees with protection against skin contact with chemicals.

2. List all the chemicals against which protection is sought and estimate the wearing time requirement for gloves (eg all day, few hours, periodically for minutes.)

3. Determine from MSDS and other sources the known consequences of skin contact with chemicals to be used (eg sensitization, dermatitis, systemic poisoning, skin absorbable).

Glove Selection: Permeability Data Available

4. Single Agents. Find the chemical against which skin contact protection is sought from among those listed in

various sources of permeation data. (see manufacturer's published literature eg. Edmont, North,, Dow, DuPont, Pioneer, AIHA Monograph) Choose gloves which provide the best performance based on breakthrough time.

5. Mixtures. For protection against chemical mixtures where component permeability data exist and components are known not be skin absorbable, systemic poisons, corrosives or sensitizers, select gloves which maximize protection against the component(s) likely to be present in greatest quantity (see appendix note 1)

6. Gloves should not be selected for protection against mixtures based on component permeability data if a mixture component is skin absorbable, a systemic poison, corrosive or sensitizer.

Glove Selection: Permeability Data not Available

7. When protection is sought against single agents or mixture component for which there is consistent toxicological evidence of high systemic toxicity, skin absorbability or irreversible effects, experimental determination of chemical permeability through gloves should be made. Gloves selected should have a least a 30 minute breakthrough time.

8. When seeking protection against chemicals for which toxicological evidence suggests a less serious hazard and

there are no permeability data available, use the following selection procedure:

-Use any two glove pairs of different composition from the permeation guide and treat the outer glove as disposable and discard it frequently, or

-Use any single glove as disposable to be discarded after completing the operation for which protection was needed or 15 minutes, whichever is sooner.

Other Selection Factors

9. After selection of gloves based on permeability data, or after selecting suitable double glove system, the following additional factors should be considered. Durability; dexterity;tactile sensitivity; friction; wearing schedule (all day, short term/frequent); cost.

10 Gloves chosen based on best permeability may not always be the best for other selection factors, but should reflect a best effort to optimize factors which are often at cross purposes. (eg. glove thickness favors reduced permeability and improved durability, but may compromise dexterity and touch)

Glove Use

11. Gloves are not intended to permit contact with chemicals, but are intended to prevent contact when accidental encounter occur. Gloves should be kept as clean as possible during use.

12. Gloves should only be used as protection against the agent considered during the selection process. Do not use gloves worn to protect skin from chemicals to clean-up broken glass or to handle unusually hot or cold objects. Gloves in contact with chemicals substantially above ambient temperatures may not provide the protection predicted by permeability data developed at another temperature.

13. The loss of tactile sensitivity during glove use may result in glove contamination without the wearer's knowledge. This increases the risk of 1. area contamination and 2. personal exposure and enhanced health effects.

14. Minimize the spread of contamination throughout the work area and beyond by making the location where gloves are to be used clearly known to all area personnel.

15. Rinse gloves frequently to minimize the spread of contamination within a designated glove-use area or to the face and mouth of the wearer. Frequent rinsing will also eliminate continued chemical challenge to gloves contaminated without the wearer's knowledge. Rinsing is recommended every half-hour and after high-potential contact operations. Even well-selected gloves will fail with continued chemical contact. The consequences could

be patching of a permeated chemical on the skin and enhanced skin or systemic effects.

Glove Reuse, Disposal, and Storage

16. When evidence of glove contact with chemicals other than those known to be skin absorbable, systemic poisons, corrosives or sensitizers is visible or otherwise known or suspected, the contaminant(s) may be washed from the glove and the glove continued in service or reused.

17. When evidence of glove contact with chemicals known to be skin absorbable, systemic poisons, corrosives, or skin sensitizers, is visible, otherwise known or suspected the glove should be discarded (see appendix note 2).

18. Do not reuse disposable gloves - discard them after completing the operation for which they were worn-more frequently if necessary (every 15 min when permeation data is not available).

19. Discard all gloves at the end of the work-week unless chemical contact is known not to have occurred.

20. If gloves are washed or otherwise cleaned with a specialized decontamination solution before disposal, contain any washings not permitted in the sewers.

21. Gloves removed for disposal need not be decontaminated. In general one contaminated glove should be peeled or stripped almost entirely off by turning the glove inside-out. Before removing it completely, use the

partially removed glove as protection while similarly removing the second glove. A container should be ready to receive contaminated gloves for proper water disposal.

22. Before reusing gloves, 1. wash the outside with soap and water, 2. remove the glove from the hand without mechanically stressing the glove. 3. rinse the glove inside and out. 4. dry the glove thoroughly and store it in a clean place. The washing procedure should not be used for water soluble gloves (eg PVA).

23. Gloves known or assumed to be contaminated to the extent that their washings would not be permitted in the sewer should be discarded in accordance with proper disposal procedures.

24. Washing gloves with solvent (eg acetone) may have unpredictable effects on the elastomer's ability to protect when gloves are reused, so reuse of solvent washed gloves is not recommended.

Note 1 - Protection against mixtures

The limitation discussed below concerns direct application of single agent permeability data on mixtures of these chemicals. Research indicated that for mixtures which show no component adverse synergism towards glove material (mixture permeability no worse than predicted component permeability) the permeation rate of these

mixtures will be directly proportional to volumetric concentrations of each solvent. This behavior cannot be predicted without conducting permeability studies but may be assumed without serious consequences for less hazardous chemicals. For protection against mixtures which do not contain hazardous chemicals you may select gloves which maximize protection against the component present in greatest concentration.

When protection is required against mixtures containing at least one of the hazardous materials (skin absorbable, systemic poison, corrosive or sensitizer), it is not reasonable to assume that there are no component adverse synergistic effects making mixtures more permeable than expected based on known component permeability. In this case a glove should not be selected until the permeability of the mixture has been determined experimentally and found acceptable.

Note 2 - Effect of Glove Washing

Most glove permeability data has been developed for single agents in continuous contact with glove material. When a glove is contaminated and then washed, some of the chemical which began to permeate the glove will continue toward and may reach the hand. For less hazardous chemicals continued use of a contaminated but washed glove

in not expected to pose a serious hazard. For materials known to be skin or systemically hazardous continued use of a contaminated but washed glove could pose a more serious hazard and is not recommended.

As stated in paragraphs 15 and 16, frequent rinsing of gloves worn for extended periods will minimize area contamination, glove permeation, and skin contact resulting from glove contamination which occurs without the worker's knowledge. This work practice is strongly recommended because 1. area contamination eg., workbench, equipment, desk, telephone, etc) can have serious consequences to the unprotected worker who is exposed later and 2. chemical breakthrough while the glove is in long term use can lead to enhanced absorption and a more serious health problem than the same exposure to even the ungloved hand (patch effect).

APPENDIX B

PREPARATION OF CALIBRATION SOLUTIONS

Standards of the pesticide compound were obtained from the CIBA-GEIGY Company. A stock concentrated solution was prepared with toluene. A small portion of this stock solution was then diluted with toluene for each calibration concentration solution used for the curve. The calibration concentrations used for the calibration curve were:

25 ppm
50 ppm
100 ppm
250 ppm
500 ppm
1000 ppm
2500 ppm
10000 ppm

To prepare the calibration solutions the stock solution was prepared first using the density and purity of the standard. For example, if the purity of the standard was 99.61% and the density was 1.116 g/ml, then to make 100 ml of a 10000 ppm stock solution:

10000 ppm = 10000 mg/l = 10000 mg/1000 ml = 1 g/100 ml

so 1 gram of compound is needed for 100 ml to make 10000 ppm stock. Multiplying the 1 gram by the density of the compound gave the liquid volume of the standard necessary for the desired concentration.

1 g x 1 ml/1.116 g = 0.896 ml

To correct this amount for purity the following correction was made:

0.896 ml/ .9961 = .8995 ml or 899.5 μl

The final calculation determined that 899.5 μl of the standard solution mixed with toluene to volume in a 100 ml flask will be a 10000 ppm concentration.

To calculate the amount of the stock solution needed to make the other calibration solutions:

$$x\ (conc_i) = (vol_f)\ (conc_f)$$

where i = initial; f = final

For example, to make a 10 ml 5000 ppm solution:

5000 ppm = (x) (10000) = (10 ml) (5000) = 5.0 ml

Therefore, 5.0 ml of stock solution was placed into a 10 ml volumetric flask and filled to volume with toluene. All other dilutions were calculated in this manner.

Then 4 μl of each solution was injected into the gas chromatograph (repeated once) using the previously defined standard parameters. The peak areas were averaged and then regressed against concentration where the resulting regression line and equation was used as the calibration curve.

Calibration curves for diazinon, metolachlor and atrazine follow. The data and predicting equation are presented in Table XII. Plots of the data appear in Figures 11, 12 and 13.

Table XII

Calibration Curve Data and Regression Results

Conc (ppm)	Average Integrator Area		
	Atrazine	Diazinon	Metolachlor
0	0.0	0.0	0.0
25	0.0	0.0	152.0
50	194.0	485.0	678.0
100	648.5	799.0	1504.0
250	1662.5	1804.5	3676.5
500	5033.0	4353.0	13068.0
1000	11375.0	9359.5	-
2500	34285.0	20797.0	65558.0
5000	57841.5	39834.0	127105.5
10000	135646.0	77490.0	282324.0
R^2	0.9953	0.9992	0.9979
Coefficient	13.34	7.83	27.59

Calibration Predicting Equations

Atrazine	$y = 13.34x + 0$
Diazinon	$y = 7.83x + 0$
Metolachlor	$y = 27.59x + 0$

Figure 11

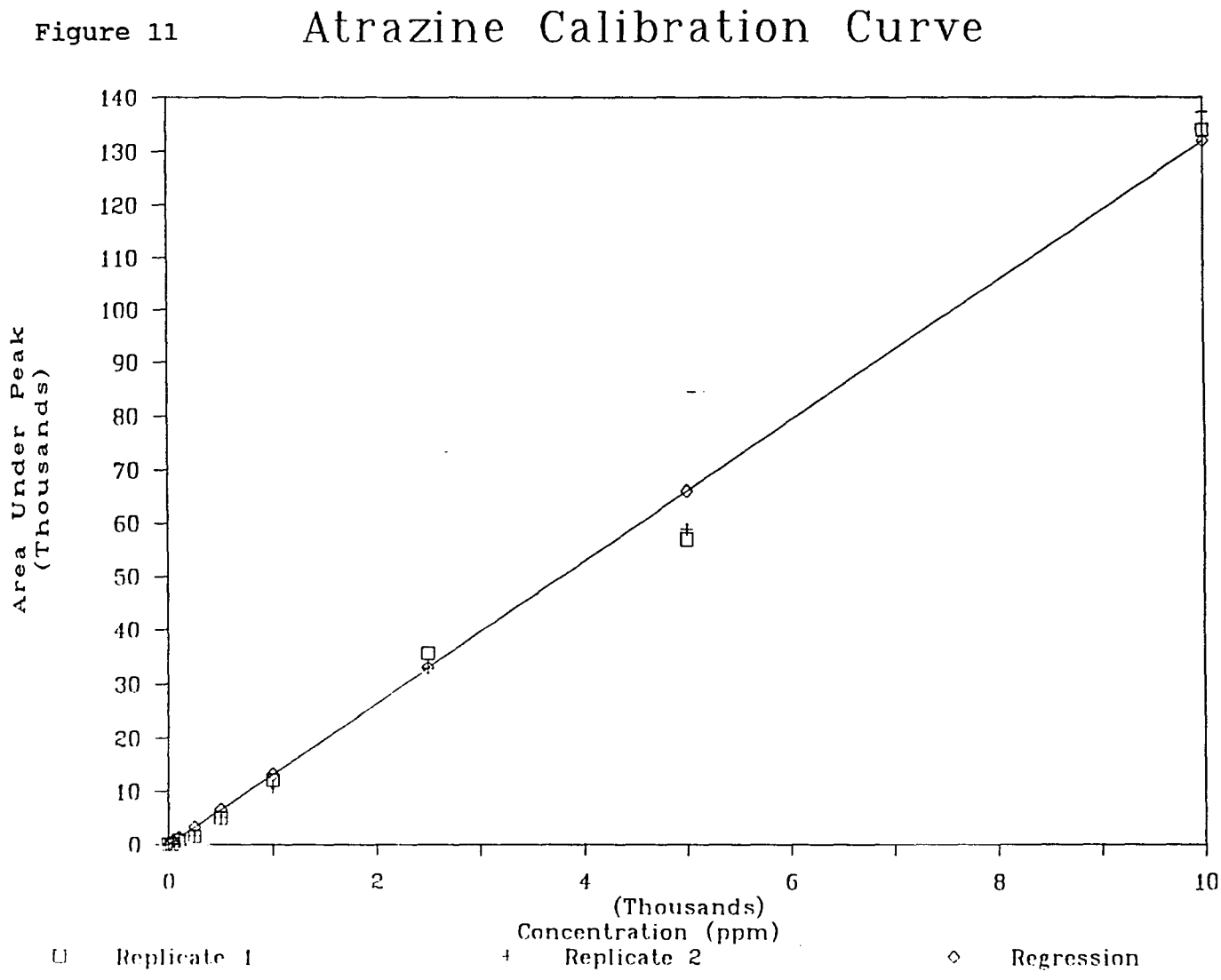

Atrazine Calibration Curve
Area Under Peak (Thousands)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
Concentration (ppm) (Thousands)
Replicate 1
Replicate 2
Regression

Figure 12

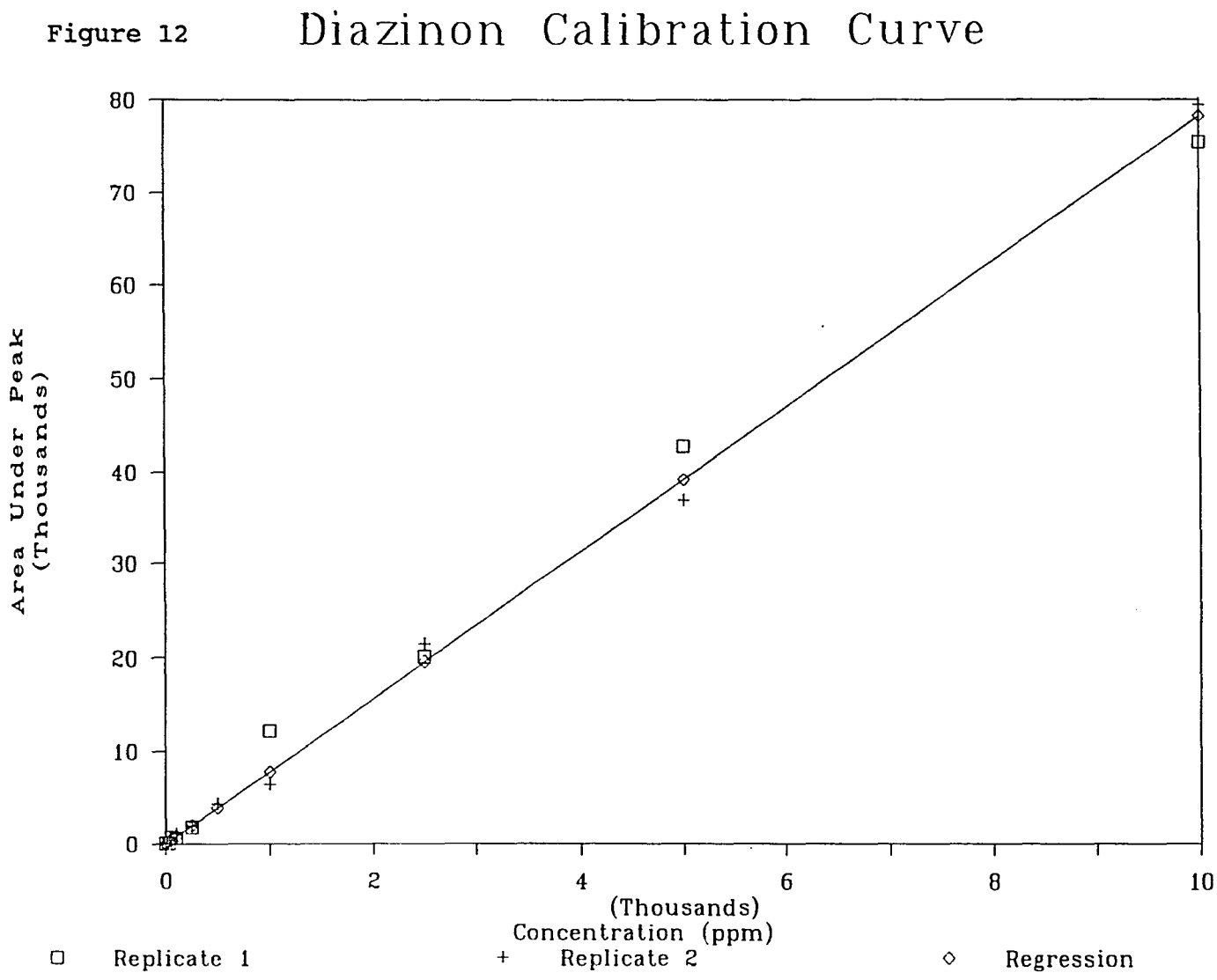
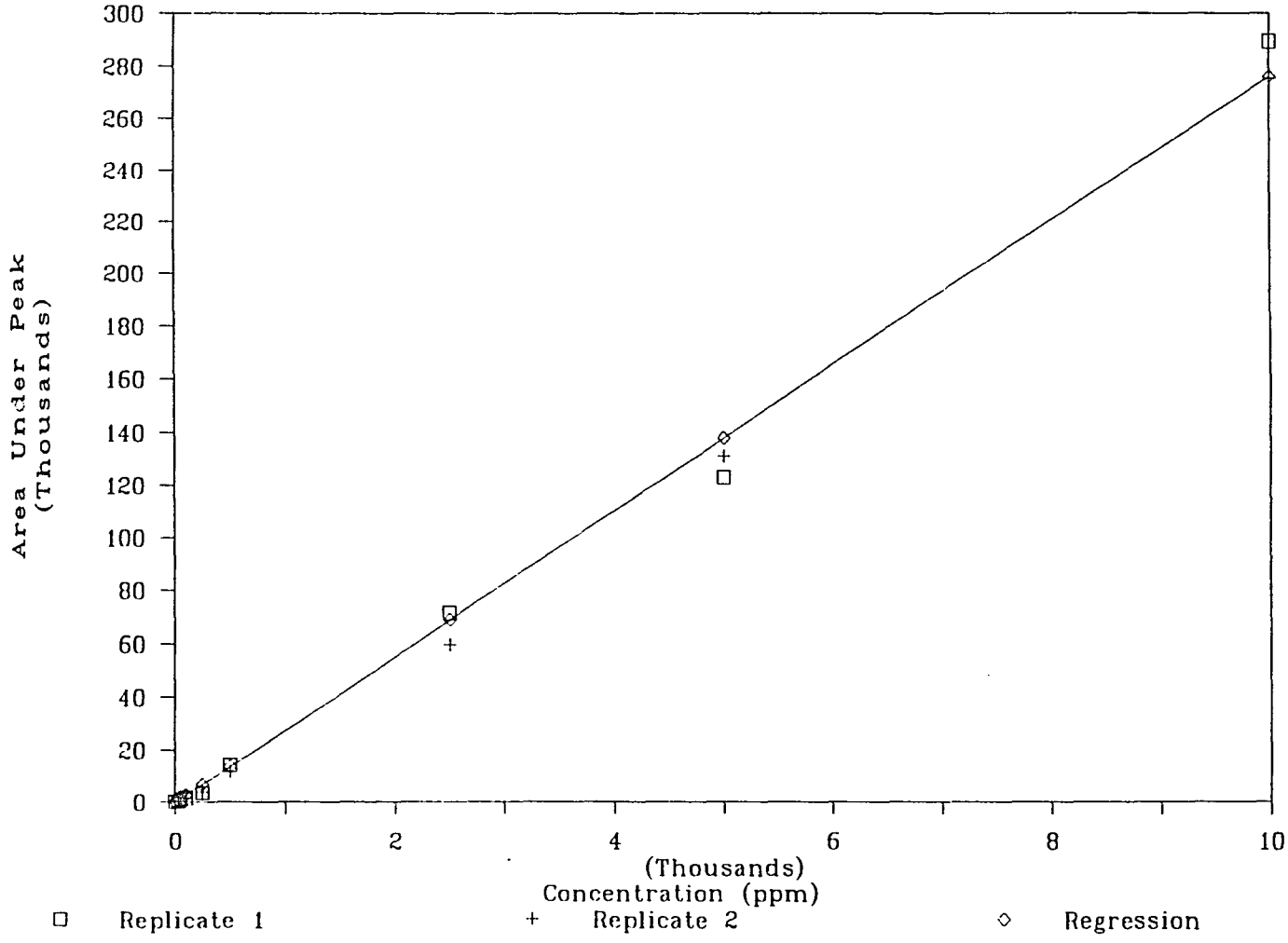

Diazinon Calibration Curve
Area Under Peak (Thousands)
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
(Thousands)
Concentration (ppm)
Replicate 1
Replicate 2
Regression

Figure 13 Metolachlor Calibration Curve



APPENDIX C

SOLVENTS FOR SOLUBILITY PARAMETER DETERMINATION

Solvent	Solubility Parameter $(J/cc)^{1/2}$			
	D	P	H	S
2,2,4-trimethyl pentane	14.1	0.0	0.0	14.1
1-octane	15.0	0.0	0.0	15.0
4-methyl-2-pentanone	15.3	6.1	4.1	17.0
ethyl chloride *	15.7	6.1	2.9	17.1
1,1,1-trichloro-ethane	16.8	4.3	2.0	17.5
xylene	17.6	1.0	3.1	17.9
3-pentanone *	15.8	7.6	4.7	18.2
ethyl acetate	15.8	5.3	7.2	18.2
benzene	18.4	0.0	2.0	18.5
chloroform	17.8	3.1	5.7	18.9
cyclohexanone	17.8	6.3	5.1	19.6
2-ethoxyethyl acetate *	15.9	4.7	10.6	19.7
dichloromethane	18.2	6.3	6.1	20.2
carbon disulfide	20.5	0.0	0.6	20.5
2-nitropropane	16.2	12.1	4.1	20.6
2-butoxythanol	16.0	5.1	12.3	20.8

Solvent	Solubility Parameter $(J/cc)^{1/2}$			
	D	P	H	S
1-octanol	17.0	3.3	11.9	21.0
benzaldehyde	19.4	7.4	5.3	21.4
acetophenone	19.6	8.6	3.7	21.7
pyridine	19.0	8.8	5.9	21.8
epichlorohydrin	19.0	10.2	3.7	21.9
dimethyl phthalate	18.6	10.8	4.9	22.1
nitrobenzene	20.0	8.6	4.1	22.2
cyclohexanol	13.8	8.6	15.3	22.3
acetic anhydride	16.0	11.7	10.2	22.3
aniline *	19.4	5.1	10.2	22.5
2-ethoxyethanol	16.2	9.2	14.3	23.5
furfuryl alcohol	17.4	7.6	15.1	24.3
2-furaldehyde	18.6	14.9	5.1	24.4
acetonitrile	15.3	18.0	6.1	24.4
1-propanol	16.0	6.8	17.4	24.6
dimethyl formamide	17.4	13.7	11.3	24.9
nitromethane	15.8	18.8	5.1	25.1
diethylenetriamine	16.7	13.3	14.3	25.7
methyl sulfoxide	18.4	16.4	10.2	26.7
triethylene glycol	16.0	12.5	18.6	27.5
1,4-dioxane	20.5	19.0	1.8	28.0
2-pyrrolidinone	19.4	17.4	11.3	28.4
1,3-butanediol	18.0	8.4	21.0	28.9
ethylene carbonate *	19.4	21.7	5.1	29.6

Solvent	Solubility Parameter $(J/cc)^{1/2}$			
	D	P	H	S
hydracrylonitrile	17.2	18.8	17.5	31.0
ethanolamine	17.2	15.6	21.2	31.4
ethylene glycol	17.0	11.0	26.0	33.0
formamide	17.2	26.2	19.0	36.7

* Solvent not available

APPENDIX D

SOLUBILITY PARAMETER WEIGHT GAINS

Solvent	Average Percent Weight Gain of Butyl Rubber
2,2,4-trimethyl pentane	123.3
1-octane	91.7
4-methyl-2-pentanone	22.8
ethyl chloride *	---
1,1,1-trichloro-ethane	58.6
xylene	291.5
3-pentanone *	---
ethyl acetate	8.9
benzene	96.7
chloroform	386.4
cyclohexanone	33.7
2-ethoxyethyl acetate *	---
dichloromethane	70.9
carbon disulfide	229.7
2-nitropropane	24.9
2-butoxythanol	0.7

Solvent	Average Percent Weight Gain of Butyl Rubber
1-octanol	7.2
benzaldehyde	20.7
acetophenone	7.0
pyridine	8.8
epichlorohydrin	19.0
dimethyl phthalate	6.5
nitrobenzene	7.2
cyclohexanol	0.0
acetic anhydride	3.0
aniline *	---
2-ethoxyethanol	0.0
furfuryl alcohol	2.4
2-furaldehyde	4.1
acetonitrile	1.6
1-propanol	2.6
dimethyl formamide	3.8
nitromethane	2.2
diethylenetriamine	3.3
methyl sulfoxide	2.5
triethylene glycol	1.9
1,4-dioxane	33.6
2-pyrrolidinone	4.6
1,3-butanediol	3.0
ethylene carbonate *	---

Solvent	Average Percent Weight Gain of Butyl Rubber
hydracrylonitrile	1.0
ethanolamine	3.5
ethylene glycol	0.0
formamide	13.6

* Solvent not available